

*94-1 Research and Development Project
Lead Laboratory Support*

*Status Report
October 1–December 31, 1996*

Los Alamos
NATIONAL LABORATORY

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*94-1 Research and Development Project
Lead Laboratory Support*

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*Compiled by
Nora A. Rink*

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94-1 RESEARCH AND DEVELOPMENT PROJECT LEAD LABORATORY SUPPORT

**Status Report
October 1–December 31, 1996**

**Compiled by
Nora A. Rink**

ABSTRACT

This status report is published for Los Alamos National Laboratory 94-1 Research and Development (R&D) projects. The Department of Energy Office of Environmental Management (DOE/EM) funds these projects in order to support the storage or disposal of legacy plutonium and plutonium-bearing materials that resulted from weapons production throughout the DOE complex.

This report summarizes status and technical progress for Los Alamos 94-1 R&D projects during the first quarter of fiscal year 1997.

INTRODUCTION

This is the fifth status report published for Los Alamos National Laboratory 94-1 Research and Development (R&D) Project Support. The Department of Energy Office of Environmental Management (DOE/EM) funds these projects in order to support the storage or disposal of legacy plutonium and plutonium-bearing materials that resulted from weapons production throughout the DOE complex.

Descriptions and milestones for fiscal year 1997 (FY97) Los Alamos 94-1 R&D projects are found in report LA-13261-PR, *94-1 Research and Development Project Lead Laboratory Support Technical Program Plan* (in press). Fig. 1 presents the work breakdown structure for this effort. This report for the first quarter of FY97 reports status and technical progress for funded Los Alamos 94-1 R&D projects.

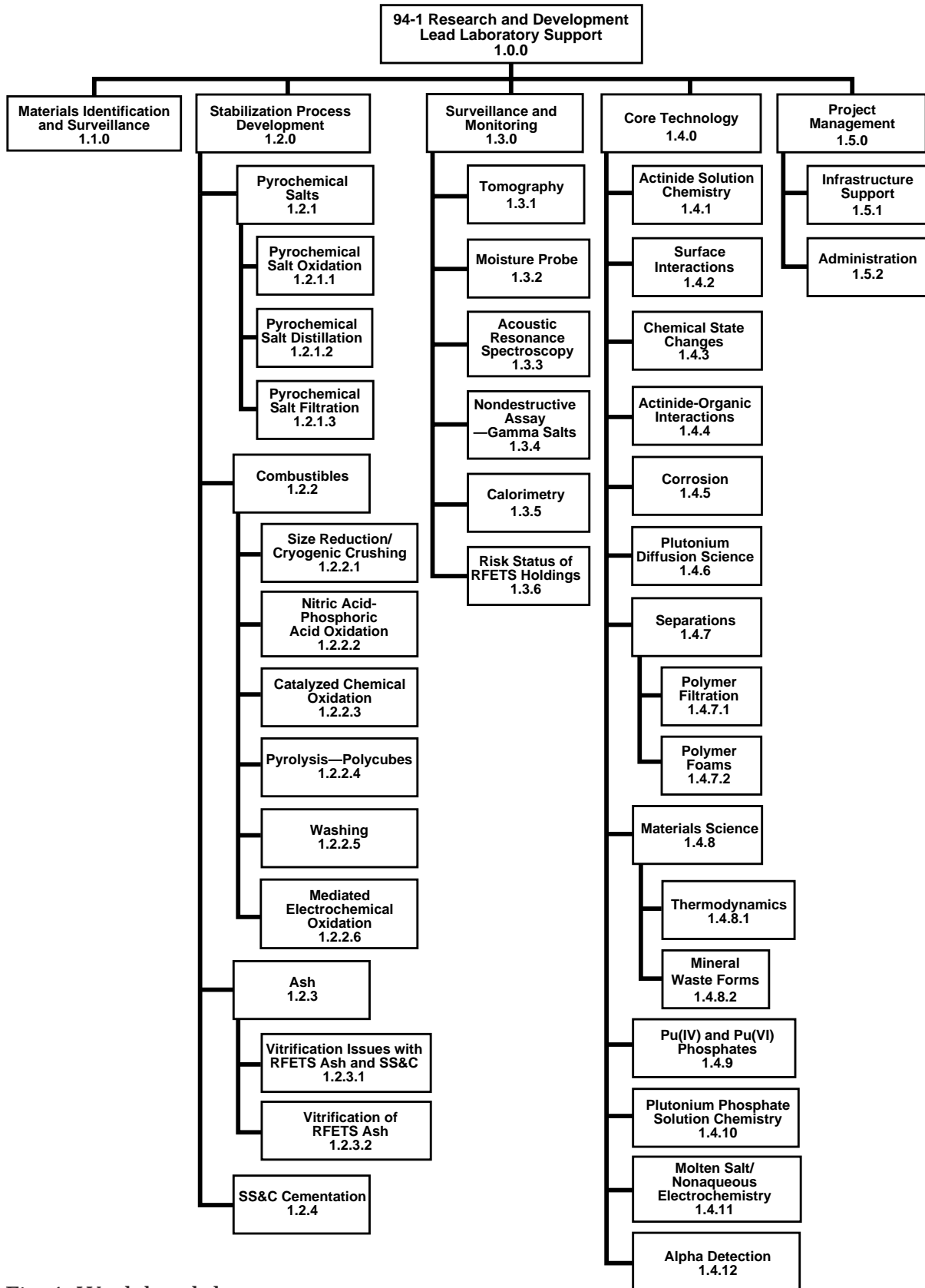


Fig. 1. Work breakdown structure.

Materials Identification and Surveillance

Principal Investigator: David Horrell

Task Description. Objectives of the Materials Identification and Surveillance (MIS) Project are (1) to identify materials to be stored in containers that meet the criteria of DOE-STD-3013 and (2) to determine the processing necessary to stabilize these materials. Representative plutonium oxide (PuO_2) materials destined for storage specified by DOE-STD-3013 will be shipped to Los Alamos where they will be characterized and their storage behavior will be determined. The MIS working group is composed of individuals from Rocky Flats Environmental Technology Site (RFETS), Babcock and Wilcox Hanford Company (BWHC), Savannah River Site (SRS), and Los Alamos National Laboratory.

Status/Accomplishments. The MIS working group met in October 1996 for a fiscal-year-end review and in December 1996 for a meeting focusing largely on thermal modeling. The working group has approved two MIS project plans: (1) Materials Identification and Surveillance Project Plan and (2) Los Alamos Comprehensive Experimental Plan: Materials Characterization and Shelf-Life Surveillance Studies, Kinetics Studies, and Corrosion Studies.

Los Alamos personnel have fabricated and nonradioactively tested the puncturing device for gas-sampling

food-pack cans. Tests on nine cans from Hanford Site should begin in January 1997 at Los Alamos.

This summary reports progress on selected MIS project tasks for the first quarter of fiscal year 1997. The summary concludes with a brief report of the work to date on thermal modeling. This work, conducted by the Nuclear Systems Design and Analysis Group at Los Alamos, was featured in a presentation to complex-wide DOE personnel at RFETS on December 17, 1996.

RFETS Material Shipment. RFETS personnel plan to ship the first 13 items to Los Alamos in April 1997. Los Alamos personnel have been working with the RFETS packaging group to ensure that RFETS will have the necessary operating procedures in place to package the DOE Standard 9968 shipping container, the only shipping container available for these items. We provided the packaging group with an approved Los Alamos packaging procedure and helped the group obtain a container from SRS. Anticipating a shipment of containers from the Mound Facility, we have reserved containers for RFETS material. We have told the group that we are available to help package, if necessary. RFETS personnel are preparing a list of the specific items to be shipped. When we receive the list,

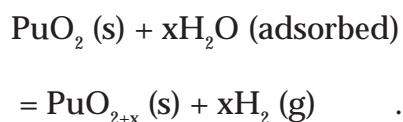
we can begin work on the shipper/receiver agreement.

The Nuclear Materials Management and Control Group at the Los Alamos Plutonium Facility has released the nine Hanford gas-sampling food-pack cans for processing.

Oxide Studies

PuO₂-H₂O Reaction. Studies of the chemistry and kinetics of the reaction between water (H₂O) and PuO₂ are currently under way at Los Alamos. The objective of these studies is to consolidate information for assessing potential hazards associated with handling and storage of PuO₂. Potential difficulties associated with oxide storage arise primarily from the oxide adsorbing molecular species from the atmosphere. Radiolysis and chemical reaction of adsorbates during oxide storage may produce noncondensable and reactive gases, which can lead to high-pressure conditions in storage containers.

The results of our recent experiments indicate that adsorbed water may react with the dioxide to form hydrogen gas and a hyperstoichiometric oxide:



In subsequent microbalance and pressure, volume, temperature (PVT) experiments, we used x-ray powder diffraction to measure the lattice constant of the oxide product as a function of reaction time, storage temperature, and hydrogen generation. The activation energy for

the above reaction, 10 kJ/mole, was calculated from an Arrhenius plot derived from three microbalance and two PVT experiments.

With the PVT apparatus, we measured reaction rates twice at 300°C and once at 350°C. We have constructed another PVT apparatus and are currently determining reaction rates in the temperature range of 100°C–350°C.

X-Ray Analysis of an Impure Mixture of Uranium and Plutonium Oxides. Los Alamos researchers examined samples of the mixed oxide PUUOXBC05 item by x-ray powder diffraction. We sampled the material as received, after firing in air at 650°C, and then after firing again at 950°C. We found samples at these three conditions to be Pu_{0.82}U_{0.18}O_{2+x} mixed with small amounts of cupric oxide (CuO) and magnesium oxide (MgO). The lattice contraction upon firing indicated that a substantial amount of uranium was oxidized to +5. The oxygen stoichiometry could not be determined quantitatively; however, the value of x lies between 0 and 0.1.

Thermochemical Modeling. Based on our evaluation of impure oxide, item ATL27960 (described later), we have decided that further studies are needed to characterize the chemistry that occurs during calcination. Thermochemical modeling could be a useful tool for predicting such behavior under a variety of conditions. Los Alamos researchers have selected two modeling programs. We are currently assessing thermodynamic data for these programs.

Supercritical Carbon Dioxide

Extraction. Los Alamos researchers conducted preliminary experiments to evaluate the ability of supercritical carbon dioxide (CO_2) to remove adsorbed water from a pure oxide surrogate (zirconium oxide [ZrO_2]), pure PuO_2 (sample PEOR3258), and an impure PuO_2 (sample ATL27960). Of particular interest are the results for the impure oxide. These results, presented in a Los Alamos report,¹ are summarized as follows.

The weight loss measured by loss on ignition (LOI) for the impure PuO_2 (sample ATL27960) was 0.97 mass %, which exceeds the specified maximum of 0.5 mass % set forth in DOE-STD-3013. However, the weight loss measured by real-time extraction was 0.025 mass %, which is well within the specifications. Because this impure oxide sample had been previously subjected to a high-temperature thermal stabilization treatment, only water that was readsorbed before packaging should have been volatilized during the LOI analysis. The large weight loss actually measured by LOI indicates that low-boiling-point inorganic compounds such as sodium and potassium salts, as well as lead salts, were being driven off, giving an erroneously high weight loss.

Our preliminary conclusion, therefore, is that an LOI measurement alone, without an accompanying means for identifying the volatilized species, cannot be relied upon to provide verification of thermal stabilization. The total weight change measured

gravimetrically on the impure oxide after extraction was positive, indicating that CO_2 had been incorporated into the sample. It is our opinion that the alkali and alkaline earth oxides (such as MgO , sodium oxide [Na_2O], and potassium oxide [K_2O]) contained in the sample were converted to carbonates. We will verify this with x-ray diffraction analyses on these post-extraction samples. If indeed it turns out that some carbonation occurred, it is of no detriment to the DOE-STD-3013 acceptance criteria.

Further work on impure PuO_2 is proceeding as follows:

- We are beginning to conduct extraction experiments on crystalline, inorganic hydroxide and hydrate compounds to demonstrate that supercritical CO_2 can remove water that is more tightly bound than adsorbed water. If hydroxides and hydrates can be decomposed to anhydrous salts, this will prove that adsorbed water can be completely removed.
- We will upgrade the supercritical extraction apparatus to allow for quantitative, simultaneous, real-time analysis of water and hydrocarbons. We have identified the necessary equipment and are currently in the design phase of the upgrade.

- We are currently conducting extraction experiments on ceric oxide (CeO_2), which is a more commonly used surrogate for PuO_2 than is ZrO_2 . We will run a series of pure and impure plutonium oxide samples, intentionally spiked with a known amount of predetermined organic compounds. These experiments are designed to determine the ability of supercritical CO_2 to extract these organic compounds.

Evaluation of Items

Impure Oxide—Item ATL27960. Los Alamos researchers have compiled a report on the characterization of properties relevant to storage of an impure PuO_2 (74 mass % plutonium) in accordance with DOE-STD-3013.² Methods used to characterize the oxide after calcination at selected temperatures include surface-area analysis, LOI measurements, elemental analysis, moisture readsorption measurements, and quantitative supercritical CO_2 extraction of adsorbed water. Significant decreases in the LOI and surface area occurred as the oxide was calcined at progressively increasing temperatures.

Our studies indicate that supercritical fluid extraction (SFE) using CO_2 as the solvent is an effective method for removing adsorbed water from oxides (see previous discussion). We have demonstrated the efficacy of this method to determine water content, and our experimentation continues.

We continue investigations to see whether these impure materials are

storable after firing at 950°C for 2 h, even though these materials do not pass the LOI test. Additional studies are needed to identify volatile species removed during calcination, to evaluate the use of a longer calcination period for meeting the DOE-STD-3013 0.5 mass % LOI requirement for storage, to define the chemical properties of the impure oxides, and to fully determine the capabilities of SFE.

We will continue studies on the impure oxide items received from other sites.

Mixed Oxide—Item PUUOXBC05.

Examination of this plutonium oxide and uranium oxide mixture was essentially completed in December 1996. We are compiling a report on our experimental results and analyses.³ The as-received powder, which had a dark brown color, was 43.81 wt % plutonium oxide and 17.77 wt % uranium oxide.

Los Alamos researchers conducted two thermal-desorption mass-spectrometry (TDMS) experiments on item PUUOXBC05. The first experiment was run from room temperature to 950°C over 7 h with a 1-h soak at 950°C . We took mass spectrometry readings (atomic mass unit [amu] 1 to 150) every 15 min throughout the run. We recorded the temperature and pressure on computerized data acquisition equipment. The second experiment was run from room temperature to 950°C over 5 h with a 2-h soak at 950°C . We took mass spectrometry readings every 30 min. Both experiments were run under dynamic vacuum conditions.

Preliminary results from the first experiment show four phases of activity. The first is between 180°C and 240°C, where the major outgassing species are hydrogen, H₂O, carbon monoxide (CO), CO₂, oxygen, and ethane. We also observed small quantities of unidentified species. The second phase begins at approximately 500°C and ends at 560°C. The outgassing species are the same as those in phase 1, with the exception that many of the minor species are no longer present and oxygen becomes a major species. The third phase is a brief spike at approximately 580°C, with the same species that we observed previously. The last phase is between 780°C and 840°C. The major species are CO₂, CO, H₂O, hydrogen, and hydrogen chloride (HCl). Numerous minor species were not identified. At higher temperatures, the gas concentration drops off until test termination. We have not yet evaluated mass spectra data for the second run.

The calculated LOI for the two TDMS runs is 11.588%. These experiments were done under dynamic vacuum conditions, and the LOI results are substantially higher than those reported for the tests done in static air. Because our experiments are not representative of the processing method used in air, we discourage direct comparison.

We performed characterization analyses on item PUUOXBC05 at three

conditions—as-received, after calcining at 600°C, and after calcining at 950°C. The characterization analyses included

- measurements of weight changes;
- water absorption measurements;
- uranium and plutonium isotopic measurements;
- uranium and plutonium assays;
- LOI measurements;
- particle and surface area analyses; and
- measurements of impurity concentration.

Tables 1 and 2 present selected data from our characterization analysis.

Plutonium, nickel, calcium, copper, magnesium, and zinc concentrations increased after the 600°C calcining step, and their concentrations decreased after the 950°C calcining step. Lithium and carbon were the only elements whose concentration decreased after both the 600°C and the 950°C calcining. Uranium was measured only in the as-received material. LOI measurements show a steady decrease as the calcining temperature is increased (see Table 2). The LOI value for the 1000°C calcined powder is 0.4 wt %; thus this powder meets the DOE-STD-3013 LOI storage criteria.

Table 1. Uranium and Plutonium Assays and Impurity Concentrations in Mixed Oxide Item PUUOXBC05

Property	As-Received	Calcined at 600°C	Calcined at 950°C
Uranium	17.77 wt %	—*	—*
Plutonium	43.81 wt %	49.65 wt %	48.85 wt %
Potassium	0.25 wt %	0.26 wt %	0.1 wt %
Sodium	0.15 wt %	0.14 wt %	0.14 wt %
Calcium	1.6 wt %	1.9 wt %	1.6 wt %
Copper	6.0 wt %	9.0 wt %	1.9 wt %
Magnesium	5.2 wt %	6.1 wt %	4.7 wt %
Zinc	5.7 wt %	6.1 wt %	5.4 wt %
Iron	0.16 wt %	0.15 wt %	0.17 wt %
Lithium	330 µg/g	200 µg/g	175 µg/g
Nickel	365 µg/g	495 µg/g	450 µg/g

* These measurements were not taken.

Table 2. LOI Results for Mixed Oxide Item PUUOXBC05

LOI Conditions	As-Received (wt %)	Calcined at 600°C (wt %)	Calcined at 950°C (wt %)
1000°C for 2 h	6.37	1.67	0.40
900°C for 2 h	5.08	1.85	0.17

Laser-Induced Breakdown

Spectroscopy. Los Alamos researchers are conducting experiments with nonradioactive laser-induced breakdown spectroscopy (LIBS) and Raman spectroscopy (RS) systems. The experiments, which involve filling a storage container with various gas compositions, are designed to optimize the detection of gas composition changes and trace amounts of gas. The nonradioactive LIBS experiments have been delayed

because of equipment failure (the detector and controller). We returned the equipment to the manufacturer for repair. We recently received the repaired equipment, and experiments can now resume.

Glovebox moves for the Advanced Recovery and Integrated Extraction System (ARIES) at Los Alamos are delaying setup of the LIBS system at building PF-4 of the Los Alamos Plutonium Facility.

Experimentation on British Nuclear Fuels, Ltd., Containers. Los Alamos researchers have designed modifications to the British Nuclear Fuels, Ltd., (BNFL) storage vessel in order to obtain real-time PVT measurements while storing pure PuO_2 and metal. These measurements will be used in planning and evaluating temperature-driven oxide reaction kinetics experiments and to validate thermal modeling. We presented our experimental setup to the MIS working group at the December 17–18 meeting at RFETS. While the BNFL container is not yet generally available, we are ordering several full sets of BNFL prototype inner, outer, and convenience containers for expedited delivery. We have prepared an experimental plan for the PVT measurements.

We will also study alpha metal phase changes during thermal cycling through the transition temperature. We will study possible can deflection caused by metal expansion at temperatures up to 250°C . SRS is providing us with BNFL prototype containers for this experimentation.

Thermal Analysis of Plutonium Materials in BNFL Containers.

Plutonium materials, including both metal and oxide forms, are placed in nested stainless-steel containers for long-term storage. DOE-STD-3013 provides criteria for packaging plutonium metals and oxides for long-term storage, and among these criteria is a maximum temperature limit of 100°C for alpha-phase metal. Although other temperature limits are not currently specified in the standard, there is substantial interest within the

DOE complex about the temperatures that are associated with storing various material forms.

We have performed thermal analyses of materials inside BNFL containers. Materials analyzed include a plutonium ingot, two plutonium buttons, and PuO_2 powder of various densities. We assumed that the cover gas inside the container was helium for metal and air for oxide. We analyzed the following cases: (1) a single container suspended in air, (2) a single container sitting on a flat plate, (3) a single container in a storage drum, and (4) an array of storage drums in vault cabinets. These external conditions for the container represent idealized situations that may exist from the time the container is loaded with the plutonium material until it is placed in permanent storage. We based these configurations on the interim storage system at RFETS. We also ran a variety of sensitivity cases, including changes in power and cover gas. In all cases, the final heat-sink temperature was 26.7°C .

Based on a fully loaded container with plutonium metal (4.4 kg generating 15-W decay heat), calculated maximum temperatures indicate that the current BNFL container design leads to metal temperatures that approach the 100°C limit for the container in air and that vault storage systems can drive the temperature of the stored metal beyond that limit. Although there is no specified temperature limit for oxide, PuO_2 in the BNFL container system can far exceed 100°C . Another observation from our results is that the outside of

the container is generally in excess of 37.8°C.

We are preparing a Los Alamos report describing all of the thermal-analysis results.⁴

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***Stabilization Process Development:
Pyrochemical Salts—Pyrochemical Salt Oxidation***

Principal Investigator: James McNeese

Task Description. This project focuses on developing chemical oxidation approaches to treating spent pyrochemical salts. The objective of the project is to mitigate all safety concerns regarding interim on-site storage of these pyrochemical salts, especially at Rocky Flats Environmental Technology Site (RFETS).

Currently, Los Alamos National Laboratory researchers are focusing on optimizing the oxidation process that prepares feed for the salt distillation process. We will perform parametric studies to determine the minimum amount of chemical oxidant necessary to ensure that (1) the oxide heel from the distillation process has the maximum special-nuclear-material concentration and (2) the distilled salt has the minimum amount of actinide. These studies continue previous work in which we developed chemical oxidation parameters for electrorefining, molten salt extraction, and direct oxide reduction salts to stabilize pyrochemical salts in standard pyrochemical furnaces.

Crucibles from pyrochemical processes exhibit the same reactive characteristics as residue salts do. In a development effort, we will investigate stabilization of crucibles

followed by maximum plutonium removal and recovery.

Another of our efforts in fiscal year 1997 will be to determine the effectiveness of liquating the pyrochemical salts after oxidation. This effort will help us determine the feasibility of a settling technique as a method of decreasing the amount of salt feed that requires distillation.

Status/Accomplishments. We are assessing the performance of oxidized electrorefining salts in the salt distillation process. This assessment is necessary first to ensure that the oxidized salt feed is acceptable in the still and second to minimize any adverse effects that the oxidized salts will have on the distillation process. When oxidation is coupled with distillation, primarily with the sodium chloride-potassium chloride (NaCl-KCl) salt matrix, the amount of carbonate used to oxidize the salts is critical. We have found that excess carbonate in an oxidized salt will result in foaming in the distillation equipment, causing operating difficulties. Earlier tests on small-scale distillation equipment did not exhibit the foaming phenomenon that we are now seeing in full-scale distillation equipment. The foaming could be caused by differences in equipment

design or by the higher vacuum levels and the increased distillation rates that we have achieved.

Currently, we are investigating methods of “killing” excess carbonate by adding high-surface-area titanium metal sponge. Laboratory tests have shown that this material successfully reacts titanium with carbonate in molten NaCl-KCl.

Another option that we are addressing is to use barium peroxide (BaO_2) as the oxidant in the oxidation reaction. This

material, which decomposes at a lower temperature than sodium carbonate does, may be amenable to a method in which excess BaO_2 is decomposed after oxidation by raising of the salt temperature. We will begin to test this theory as soon as we acquire the BaO_2 .

After testing these methods with nonradioactive materials, we will test them on pyrochemical salt matrices to be fed to the distillation process. We will then develop final recommendations for oxidation parameters.

Stabilization Process Development:

Pyrochemical Salts—Pyrochemical Salt Distillation

Principal Investigator: Eduardo Garcia

Task Description. Los Alamos National Laboratory personnel are demonstrating equipment designed to carry out the pyrochemical salt distillation process. The salt distillation process is designed to separate plutonium pyrochemical salts into a very lean fraction (<100 parts per million [ppm]) plutonium and plutonium oxide suitable for storage according to DOE-STD-3013. The chloride content of the pyrochemical residues is thereby converted into stable, slightly contaminated salt; and the plutonium content is separated into a homogeneous, well-characterized oxide material suitable for long-term storage.

For calcium chloride (CaCl_2) salts, we will investigate an alternate process that uses an aqueous dissolution and filtration separation.

Status/Accomplishments. During the first quarter of fiscal year 1997, Los Alamos personnel began operating the full-scale prototype distillation unit with plutonium residues. For feed material, we used three electrorefining residue salts previously oxidized by sodium carbonate (Na_2CO_3). We also performed several other experiments using uncontaminated salts. The distillation unit continues to perform as we expected, with processing times and operating parameters within the

envelope determined during testing with nonradioactive materials.

We reduced the plutonium content of the first electrorefining salt from 3.2 wt % to 0.4 ppm. This residue salt meets the criterion for disposal as low-level waste. The plutonium concentration of the distillation heel was 58%, satisfying the concentration criterion of DOE-STD-3013 for long-term storage.

The test runs using the other two electrorefining residue salts were not as successful. These two salts originated from the same parent electrorefining residue and were processed with an excess of Na_2CO_3 . The large amount of Na_2CO_3 caused the salt to foam over the crucible during heat up under vacuum. Although we eventually were able to successfully process these salts, the question of excess Na_2CO_3 must be addressed. This question will be addressed as part of the Pyrochemical Salt Oxidation Project, also described in this report.

We also performed some work on CaCl_2 direct-oxide-reduction residue salts. This process involves aqueous dissolution of CaCl_2 salts oxidized with Na_2CO_3 . After the salt is dissolved, metal oxides can be separated from the salt solution by filtration. The filtrate salt solution is

evaporated to dryness, and a solid CaCl_2 waste form is obtained.

Our previous experiments with actual residues have shown that the plutonium concentration of the final purified CaCl_2 waste is comparable with vacuum-distilled sodium chloride-potassium chloride (NaCl-KCl) salts. However, the time required to completely dissolve the salt was excessive, sometimes requiring several days. We attributed the excessive dissolution times to agglomerate formation. These agglomerates contained a mixture of insolubles and salt and greatly reduced the rate of salt dissolution. We believe that the agglomerates are forming because of the cementlike

mixture of calcium oxide, calcium hydroxide, Na_2CO_3 , and possibly calcium carbonate.

We are pursuing several avenues to overcome the slow dissolution kinetics. A change of equipment may improve the situation. Currently, a gas sparge is used to agitate the aqueous solution. We intend to substitute a stirrer to provide more positive agitation in the dissolution vessel.

A less desirable approach involves the use of dilute hydrochloric acid to neutralize the carbonates and calcium oxide. We add only enough acid to neutralize the solution; the solution never becomes acidic. Our preliminary results have shown this approach does improve the dissolution kinetics.

***Stabilization Process Development:
Pyrochemical Salts—Pyrochemical Salt Filtration***

**Principal Investigator: Bartley B. Ebbinghaus,
Lawrence Livermore National Laboratory**

Task Description. The Pyrochemical Salt Filtration Project involves testing molten salt filtration as a means to separate and stabilize actinides from spent pyrochemical salts. The process uses a porous ceramic crucible (for example, zirconia or alumina between 70% and 82% dense) as the filtration medium and is easily adaptable to existing and planned processing equipment at Rocky Flats Environmental Technology Site (RFETS).

To perform these tests, Lawrence Livermore National Laboratory (LLNL) is using its standard pyrochemical furnaces in argon atmosphere gloveboxes and its own limited supply of spent salts, primarily calcium chloride (CaCl_2) electrorefining salts that are approximately 2–5 years old. These salts are similar in composition to direct oxide reduction (DOR) salts in that they are composed primarily of CaCl_2 . Unlike DOR salts, however, the LLNL salt residues generally contain 10 to 20 wt % actinide; some plutonium trichloride (PuCl_3), which is soluble in molten CaCl_2 ; and in some cases, significant quantities of magnesium oxide (MgO) crucible. DOR salts typically contain no more than a few weight % residual actinide and no PuCl_3 , and the amount of crucible will depend upon the care

that was taken when the crucible was broken and separated from the salt. The goal of our initial work has been to demonstrate that (1) the salt can be filtered at a reasonable rate and (2) the actinides are efficiently separated from the salt.

Status/Accomplishments. Our preliminary results indicate that if the actinide content is low, the filtration proceeds readily, but if the actinide content is high, the process proceeds very slowly. Data for the four salt filtration tests are summarized in Table 3.

In the first molten salt filtration test, we removed about 69% of the salt by filtering at approximately 840°C for 2 h followed by filtering at 920°C for 2 h. Subsequent heating for 4 h at 1000°C yielded about 1% additional salt. The filtered salt was a light purple gray color, rather than white as would be expected for pure salt. Based on neutron counting, the concentrate contained about 16% actinide and the filtrate contained about 0.5% actinide. The actinide in the filtered product is presumably PuCl_3 , thus yielding the light purple color. If the salt were oxidized during filtration, we believe that the actinide content in the filtered salt would be further reduced. The residue concentrate in the filtration crucible was powdery and friable.

Table 3. Summary of Salt Filtration Tests*

Run No.	Input Feed Weight (g)	Initial Actinide Content (wt %)	Primary Heating			Secondary Heating		
			Filtration Time (h)	Filtration Temperature (°C)	Salt Removed (wt %)	Filtration Time (h)	Filtration Temperature (°C)	Salt Removed (wt %)
1	900	8	2 & 2	840 & 920	69	4	1000	1
2	635	24	4	1000	0	NA [†]	NA [†]	NA [†]
3	712	26	5	1000	9	6	1060	10
4	603.1	0.2	3 & 4	1006 & 807	28	8	902	12

* The filtration crucible used in run 4 was approximately twice as thick as those used in runs 1–3.

[†] Not applicable.

The second test was less successful because of a large amount of actinide and other refractory materials (that is, MgO crucible) in the salt. We heated the salt residue to 1000°C for 4 h, and we did not observe any salt drain through the filtration crucible. In fact, the salt did not even melt significantly, verifying that a large fraction of the residue is insoluble refractory material.

The third test was similar to the second. The feed had a large amount of actinide, which presumably plugged the pores in the filtration crucible and slowed the rate at which the salt was drained. We were able to remove only about 9% of the salt after heating 5 h at 1000°C. Heating the material to 1060°C for an additional 6 h yielded an additional 10% of salt. By observation, most of the salt appeared to be removed from the residue. The product was solid and not powdery and friable as in the first test.

In the fourth test, we tested a salt with very little actinide. This particular crucible was approximately twice as thick as the previous ones. We heated the salt first at about 1000°C for 3 h

and then at about 810°C for 4 h. This time, 28% of the salt passed through the filtration crucible. Some salt stalactites were present on the bottom of the filtration crucible, indicating that the salt was draining readily at the time it froze upon cooling. Additional heating at about 900°C for 8 h yielded an additional 12% salt. Data for the molten salt filtration tests are summarized in Table 3.

We also tested aqueous wash, using the residue concentrate from the first experiment. The crucible with the concentrate was filled with water (about 800 mL) and then suspended above a catch container. There was salt in the pores of the crucible, and it took about 4 h to dissolve enough salt out of the pores to allow the moisture to seep through. In comparison, an empty unused crucible filled with water will drain almost completely in 2 h. We allowed the solution to drain over the weekend, obtaining a sludge which we washed with about 250 mL additional water, dried, and then calcined at 600°C in air. As a result of the aqueous wash, about 71% of the nonactinide constituent was removed. The exact actinide content in the calcined product has not yet been

determined; based on the input and output numbers, however, it appears to be greater than 60%.

Our preliminary tests indicate that salt filtration may be a fast and simple process for removing salt content from salt residues with actinide content of approximately 5 wt % or less, such as RFETS DOR salts. For CaCl_2 molten salt extraction salts, which contain higher actinide content (about 20%) and soluble PuCl_3 , the salt scrub process would probably be more effective.

In further work, we will explore ways to accelerate both the molten salt and the aqueous filtration process; examples include using lower-density filtration crucibles, using tandem crucibles with varying pore sizes, and using air instead of argon atmospheres. We will also test the salt filtration process with actual DOR salt residues to better determine the actinide separation effectiveness.

***Stabilization Process Development:
Combustibles—Size Reduction/Cryogenic Crushing***

Principal Investigator: Timothy O. Nelson

Task Description. Cryogenic grinding at low temperature reduces materials in size.

Status/Accomplishments. Los Alamos National Laboratory personnel began testing and demonstrating the Task Master™ shredder received from the Franklin Miller facility in Livingston, New York. We also started work on the high-efficiency particulate air (HEPA) filter remediation project.

Franklin Miller Shredder. The Franklin Miller shredder arrived at Los Alamos National Laboratory during the first quarter of fiscal year 1997 and has been assembled and prepared for testing. We have shredded plastic bottles, Tyvec™, and cotton coveralls. We have talked with the hydrothermal project team (whose program is now being conducted under Defense Program funding) about size requirements for the hydrothermal oxidation process. We plan to shred some material to see if the shredder will meet the hydrothermal project team's needs. Preliminary test results suggest that if the material is run through the shredder more than once, the size will be satisfactory for the hydrothermal oxidation process.

During the shredding of plastic bottles and cotton coveralls, we have learned that both require liquid nitrogen

precooling for good shredding. When the materials are warm, the plastic will tend to deform and stretch and the cotton will pack between the shredder teeth and plug the shredder. The plastic bottles tend to roll on top of the cutter blades and will need to be pushed into the blades. This task can be accomplished easily in the feed shoot. The cotton cloth will plug the shredder if fed too quickly into the cutter blades.

The shredder can be modified to fit into a glovebox, where it can be safely operated with simple safety interlocks.

We demonstrated the shredding of plastic bottles for Los Alamos waste management personnel. We also demonstrated the shredding of rubber gloves and cotton coveralls for the hydrothermal project team, which is preparing to process a new waste stream.

We will continue to shred different wastes in the Franklin Miller shredder and continue to make modifications for glovebox installation.

HEPA Filter Remediation. At a technical review meeting on October 22, 1996, we presented our filter disassembly proposal to the combustion group at Rocky Flats Environmental Technology Site

(RFETS). Our discussion determined that only the outer 1/8 in. needed to be shaved off the filters. During the meeting we agreed upon the following equipment development and tests:

Equipment Development

- Modify the 8-in. jointer by adding a rodless actuator filter feeder.
- Provide a sawdust and chip collection system.
- Provide a nail/screw countersink capability.

Test Descriptions

- Conduct endurance test of cutting plywood with carbide blades.
- Conduct endurance test of cutting particle board with carbide blades.
- Demonstrate filter running through jointer.
- Demonstrate nail and screw countersink.
- Dip filter in 12 M nitric acid and run through jointer after dry.

According to the needs of the combustion group at RFETS, we will fabricate, assemble, and test the jointer and assembly to remove wood from HEPA filters.

***Stabilization Process Development:
Combustibles—Nitric Acid-Phosphoric Acid Oxidation***

Principal Investigator: Robert A. Pierce, Savannah River Site

Task Description. The Nitric Acid-Phosphoric Acid Oxidation Project focuses on developing a system for treating radioactively contaminated organic materials. A primary objective of this project is to test and verify the applicability of the nitric acid-phosphoric acid oxidation system for combustible organic compounds contaminated with plutonium.

Associated tasks include developing a sensor for in situ monitoring of key compounds in the oxidation process, measuring plutonium fractionation during operations, measuring potential off-gas emissions, and verifying the final immobilization of the resulting acid-metal mixture.

Radioactive demonstration of the nitric acid-phosphoric acid process will complement nonradioactive pilot testing to be conducted in a mixed-waste program. These two activities will essentially complete development of the nitric acid-phosphoric acid oxidation system. The system is designed to treat combustible residues at Rocky Flats Environmental Technology Site, ^{238}Pu at Savannah River Site (SRS), and other commercial nuclear wastes.

Status/Accomplishments. SRS personnel designed, procured, and assembled a unit for radioactive

testing. This unit will be placed in a hood at the Savannah River Technology Center.

SRS personnel completed nonradioactive work on iron phosphate glass to identify a glass composition to be used in immobilizing radioactive solutions. The glass uses 33% ferric oxide (Fe_2O_3), 5.5% sodium oxide (Na_2O), 2.5% strontium oxide (SrO), and 59% phosphorus pentoxide (P_2O_5). The American Society for Testing and Materials (ASTM) standard product consistency test for leachability showed the final form of the glass to be approximately 10 times more durable than the Defense Waste Processing Facility borosilicate glass. This assumption is based on comparing the Na_2O concentrations and leachability of both glasses. Na_2O is the only component present in both glasses in comparable amounts, and Na_2O is one of the most leachable components present in either glass.

SRS researchers have conducted preliminary work with a spectrophotometer, and results look promising. In tests using mixtures of known amounts of nitric acid in phosphoric acid, measured values closely matched those of reference samples. Further experimentation showed that the approach proposed

by SRS has high potential for working in situ, in which case a small sidestream would be withdrawn and diluted with a known amount of water. When tested this way, the instrument has shown an ability to measure nitric acid to within ± 0.05 M.

SRS researchers began testing with organics to determine if dissolved organics create any measuring interference or bias. This effort, however, was put on hold until FY97 funding can be obtained.

***Stabilization Process Development:
Combustibles—Catalyzed Chemical Oxidation***

Principal Investigators: Wayne H. Smith and Charles Brown

Task Description. The objective of this task is to demonstrate catalytic chemical oxidation technology, specifically the DETOXSM process patented by Delphi Research, Incorporated (DRI) of Albuquerque, New Mexico. This task includes the following major activities:

- design and configuration of the demonstration unit to provide a system ready for glovebox installation in Los Alamos National Laboratory's Plutonium Facility (TA-55);
- continuing development to evaluate final disposition of liquid effluent and spent DETOX reaction solution; and
- installation of the demonstration system and system testing on combustible plutonium residues.

Status/Accomplishments. By January 1997, Rocky Flats Environmental Technology Site will have reevaluated the baseline treatment systems planned for each type of plutonium residue that requires stabilization, including combustible residues.

Additional funding for this project has been put on hold pending the results of this reevaluation and a subsequent evaluation by the Department of Energy and the 94-1 Research and Development Project of changes in fiscal year 1997 development needs. The contract with DRI to assemble the demonstration system and test the system with nonradioactive materials is being completed and will be finished by the end of January 1997.

In December 1996, DRI completed a draft detail design report of the demonstration system. All of the equipment and parts for the demonstration system have been received, the mock glovebox has been constructed at DRI, and the system has been assembled within the mock glovebox. The procedure for system disassembly and installation in the glovebox at TA-55 has been completed. Los Alamos personnel are scheduled to perform a run-through of the system installation in January 1997. Following this run-through, the equipment will be tested with nonradioactive materials at DRI and then packaged and shipped to Los Alamos.

***Stabilization Process Development:
Combustibles: Pyrolysis of Polycubes***

Principal Investigators: Daniel J. Kathios and John J. Coogan

Task Description. Approximately 1600 uranium/plutonium/polystyrene polycubes that were manufactured for criticality studies, and are now in storage at Babcock and Wilcox Hanford Company (BWHC), represent waste that is not suitable for long-term storage.

The aim of this work is to design, test, and implement a pyrolysis system that will effectively volatilize and remove the polystyrene matrix, leaving the oxides as free-flowing powders that are suitable for either dissolution or long-term storage. The polycube pyrolysis system will operate in compliance with environmental and safety regulations and will be suitable for glovebox operations.

Tests with nonradioactive materials have shown that the Los Alamos National Laboratory pyrolysis reactor design allows for almost 100% removal of the polystyrene without the formation of tars or other constituents that could adversely affect reactor operation. After pyrolysis, the organic constituents will be oxidized with an off-gas treatment technology. Project personnel are considering secondary combustion, catalytic conversion, and silent discharge plasma (SDP) for the treatment of the pyrolysis off-gas. BWHC has selected SDP, based on an

engineering study conducted by BWHC personnel. Los Alamos work will proceed toward logical hold points for all off-gas technologies until the technical maturity of SDP for pyrolysis of polycubes can be demonstrated.

Status/Accomplishments. Los Alamos personnel completed fabrication of pyrolysis reactors, along with reactor canisters, heat shields, and canister extractors. We will add furnaces to two of the reactors for testing with the catalytic conversion and SDP pyrolysis off-gas treatment technologies.

We completed assembly of the B-Line Strut™ system for the polycube stabilization system. The pyrolysis reactor, furnace, and piping will be added to the B-Line Strut assembly with completion in mid-December 1996.

We completed assembly of the six-cell SDP unit that will permit full-scale testing when coupled with a pyrolysis reactor. We will use the test data to design a prototype production unit for implementation at BWHC.

We continued the elevated temperature testing (300°C–350°C) with the one-cell SDP unit during the first quarter of fiscal year 1997. In the fourth quarter of fiscal year 1996, testing revealed that operating the unit

at elevated temperatures greatly reduced film formation on the reactor surfaces. However, longer-term testing at these temperatures has revealed an unacceptable failure rate for the quartz material in the unit due to increased dielectric losses at temperatures above 300°C. We then constructed a ceramic cell and successfully tested it at higher temperatures with no increase in dielectric loss. We have ordered additional ceramic cells and will upgrade the six-cell prototype to ceramic dielectrics in January 1997. Design, procurement, and assembly of the SDP power supply for the six-cell system is scheduled for completion in January 1997.

We completed fabrication of the catalytic conversion units. Assembly of the first catalytic conversion test system began in late November 1996. Testing of the catalytic conversion system is scheduled to begin in January 1997.

Final design and procurement specifications for the secondary combustion unit were completed in December 1996.

We conducted a process hazards analysis session in October 1996. We have sent project personnel a draft summary of the hazards analysis for comments.

***Stabilization Process Development:
Combustibles: Washing***

Principal Investigators: Norman C. Schroeder and Moses Attrep

Task Description. The objectives of the Washing Project are (1) to remove organics such as cutting oil and solvents such as carbon tetrachloride [CCl_4] from combustible residues and (2) to stabilize finely divided plutonium metal contaminants on combustible residues. The project is divided into two portions: work with cerium surrogates and experiments with plutonium-containing surrogates. The project will involve evaluation of the advantages and limitations of the proposed residue washing technology.

Our focus is to demonstrate the washing, desorption, and plutonium stabilization unit operations of a proposed Rocky Flats Environmental Technology Site (RFETS) baseline flow sheet for combustibles contaminated with organics, solvents, and plutonium. A proposed CCl_4 extraction of the cutting oils was eliminated from the flow sheet for a variety of reasons.

The flow sheet has been rebaselined by RFETS personnel, and we have received some guidance concerning the modifications. The modified flow sheet, titled the Organic-Contaminated Combustibles Modified Baseline, includes the same process steps as those we are currently testing with the original baseline flow sheet. However, we will now coordinate our process

with the process specified in the flow sheet titled Nitrate-Contaminated Combustibles Modified Baseline. The interface between the modified baseline flow sheets is a sonic washing procedure that will separate most of the plutonium oxide from the combustible matrix. Our work scope is to develop basic information on the separation of plutonium oxide from RFETS materials by means of sonication. This assignment will extend our tasks into many of the process steps documented in the nitrate-contaminated combustibles flow sheet.

Status/Accomplishments. Several developments have caused delays in this project. For example, RFETS requested the addition of a permanent heating/cooling unit to the Parr Instrument Company reactor, resulting in a 6-week delay in the reactor delivery. The reactor installation in the glovebox at Los Alamos National Laboratory's Radiochemistry Site (TA-48) will involve Johnson Controls World Services, Inc. crews. The scheduling of these crews may also adversely impact the project schedule.

Activities continued for the installation of the Parr reactor in the glovebox at TA-48. We received the 2-gal. pressure reactor, aluminum

cooling/heating unit, and pressurized water injection system from Parr. Fig. 2 shows the 2-gal. Parr reactor. We have also received a small 300-mL pressure reactor from Parr, which is shown in the upper right quadrant of the figure. Both reactors are currently undergoing evaluation and testing with the nonradioactive surrogate. We will use the smaller reactor for small-scale testing of the plutonium metal with the surrogate.

Jona Machining in Los Alamos is manufacturing the secondary containment unit needed to enclose the reactor/heating/cooling unit in the glovebox. With the help of a mechanical fabrication technician from the Los Alamos National Laboratory Nuclear Materials Technology (NMT) Division, the glovebox preparations are under way.

We submitted a radiation work permit (RWP) for review. The RWP was required because our procedure requires the transfer of plutonium oxide (PuO_2) from the glovebox to a hood in order to evaluate the completeness of the steam oxidation stabilization. The use of hydrochloric acid (HCl) in this evaluation requires that the work be done in a hood in order to avoid corrosion of the glovebox. The RWP review has identified several environment, safety, and health (ESH) issues that need to be addressed for the start-up of a new radioactive project in a Los Alamos National Laboratory Chemical Science and Technology (CST) Division facility. The major ESH concern is the potential for contamination both during the transfer and while performing work in the hood.

Our response to ESH concerns is not a trivial process, involving the following activities, among others.

- An ESH safety officer from the CST Division Office has reviewed pressure and temperature parameters for the small- and large-scale Parr reactor experiments to be conducted in the glovebox.
- We completed a National Environmental Policy Act (NEPA) questionnaire and placed the results on the internal Los Alamos National Laboratory World Wide Web site for comments and questions. We will need to respond to any questions raised by this process.
- We are addressing the disposition of the waste from our planned work. We are negotiating to send our plutonium to NMT Division's Actinide Process Chemistry group (NMT-2) for recovery or cementation.
- Our principal investigator has been fitted for a respirator. Initially, transfer of PuO_2 from the glovebox to the hood will be performed by personnel wearing respirators until concerns of the radiation control technicians are mitigated.

All of these activities bring us closer to satisfying the ESH requirements for this project.

The rebaselined flow sheet calls for a review of current aqueous cleaning technology in conjunction with ultrasonics. We are currently performing this review. In order to

acquire technical expertise in ultrasonics, we have contacted equipment manufacturers. We have also interviewed Los Alamos Plutonium Facility personnel who performed ultrasonic work on filters containing plutonium residues. We are evaluating the scope of work sent to us from RFETS. The scope of work specifies seven tasks, which involve determination of

- how much plutonium is removed by the sonic washing process;
- how much nitrate is removed from the combustibles by either a water or caustic wash;
- a method to separate the combustible matrix from the liquid phase;
- how much organic material remains with the plutonium solids after washing;
- how much plutonium is solubilized with and without chelators present;
- how the final plutonium-contaminated liquid stream should be processed; and
- if the process is feasible on a 40-L scale, which is the planned scale for operation at RFETS.



Fig. 2. Parr 2-gal. reactor with controller, heating and cooling unit, and water injector. A 300-mL reactor for small-scale plutonium reactivity studies is located in the upper right quadrant of the figure.

***Stabilization Process Development:
Combustibles—Mediated Electrochemical Oxidation***

Principal Investigator: Wayne H. Smith

Task Description. The objective of the Mediated Electrochemical Oxidation (MEO) Project is to develop MEO as a viable technology for the treatment of combustible waste. The project's aim is to compare the applicability and utility of MEO with other treatment technologies currently under development.

Status/Accomplishments. Work on the MEO Project has slowed, pending a decision at Rocky Flats Environmental Technology Site (RFETS) concerning which combustible residue treatment technologies to pursue. By December 20, 1996, RFETS is to provide DOE with a plan to treat the combustible residues. DOE is expected to take approximately 1 month to respond to this plan. The current RFETS baseline calls for a combustible residue washing/stabilization process followed by packaging and shipment to the Waste Isolation Pilot Plant. Such a process would be labor intensive and costly.

The DOE-sponsored combustibles trade study has recommended MEO as an alternate treatment technology for at least a fraction of the residues, specifically the Full-Flo™ filters. The Los Alamos Technical Office (LATO) at RFETS supports a modified

washing flow sheet, which requires demonstration. (See the summary titled "Washing" in this report.)

Without the support of either RFETS or LATO, it is unlikely that MEO will be accepted for treating the combustible residues at RFETS, despite the DOE trade study recommendations. However, researchers at Los Alamos National Laboratory are awaiting required DOE input on the washing programs before abandoning further MEO development. In any event, we believe uncertainties in the washing programs require continued development of MEO and DETOXSM as backup technologies for at least one additional year.

As a result of the delay, however, the milestones associated with this project have slipped by approximately 4 to 6 months. In the meantime, Pacific Northwest National Laboratory is developing a balance-of-process flow sheet that will enable packaging of concentrated plutonium in containers specified by DOE-STD-3013 and treatment of liquid waste generated by MEO. Information on the amount and treatment of liquid effluent is essential for a decision to continue development of MEO.

***Stabilization Process Development:
Ash—Vitrification Issues with Rocky Flats Environmental Technology Site Ash
and Sand, Slag, and Crucible***

Principal Investigator: Gerald Veazey

Task Description. The objective of this project is to support the effort by Safe Sites of Colorado to develop a vitrified waste form for Rocky Flats Environmental Technology Site (RFETS) ash. Project tasks are (1) to determine nondestructive assay (NDA) restraints and operating parameters for a vitrified waste form and (2) to investigate use of a conventional furnace system for vitrification as an alternative to the microwave technology under study at RFETS.

Status/Accomplishments. Los Alamos National Laboratory researchers have determined a methodology for generating the samples of vitrified surrogate RFETS ash that are required for NDA experiments. We will use actual RFETS ash to prepare full-scale samples that resemble as closely as

possible the actual RFETS waste forms. The RFETS ash we will use is available in the Los Alamos Plutonium Facility (TA-55) vault.

For our NDA experiments, we will use a muffle furnace in the glovebox system at TA-55. This furnace is similar to the RFETS furnace.

We have designed the off-gas scrubber equipment for the nonactinide experiment on low-temperature furnace vitrification. We have ordered the parts and expect that the scrubber will be ready for assembly in January 1997. Pacific Northwest National Laboratory is currently preparing the statement of work for low-temperature vitrification. We have obtained the composition of RFETS ash for use in surrogate ash preparation.

***Stabilization Process Development:
Ash—Vitrification of Rocky Flats Environmental Technology Site Ash***

Principal Investigator: T. S. Rudisill, Savannah River Site

Task Description. Approximately 20 000 kilograms of incinerator ash are currently stored at the Rocky Flats Environmental Technology Site (RFETS). Vitrification has been proposed as one treatment technology to stabilize this material and produce a waste form that can be shipped. Vitrification would allow potential disposal to the Waste Isolation Pilot Plant or, by means of the can-in-can approach, in high-level-waste glass from the Defense Waste Processing Facility.

The objectives of this work are to demonstrate and optimize glass formulations and processing conditions required to vitrify the RFETS ash. Using the borosilicate and soda-lime-silicate glass formulations demonstrated during fiscal year 1996 as a starting point, Savannah River Site (SRS) researchers will use a statistically designed experimental program to address the range of elemental compositions reported for RFETS ash and to optimize the primary

processing variables (liquidus temperature and viscosity) and glass durability. The program will consist of a series of melts during which the ash and/or frit composition is systematically varied to produce the most desirable processing conditions and the most durable glass.

Status/Accomplishments. The initial vitrification experiments performed during fiscal year 1997 focus on the variability of the incinerator ash's composition. The goal of the variability study is to identify the chemical components that have the greatest effect on glass formulation (liquidus temperature, viscosity, crystallinity, etc.) and determine the loading limits for these species. SRS researchers defined a statistically designed set of experiments by systematically varying the concentration of the oxides that have the greatest influence on glass properties. The oxides and ranges of concentration are shown in Table 4.

Table 4. Oxide Concentrations Used for Variability Study

Oxide	Low Concentration (wt %)	High Concentration (wt %)
Aluminum Oxide (Al ₂ O ₃)	1	6
Calcium Oxide (CaO)	1	7
Chromium Oxide (Cr ₂ O ₃)	0.4	1
Cupric Oxide (CuO)	0.5	1.5
Ferric Oxide (Fe ₂ O ₃)	1	11
Magnesium Oxide (MgO)	1	8
Alkali (Sodium Oxide [Na ₂ O] and Potassium Oxide [K ₂ O])	0	2.4

The statistical design includes 20 experiments in which we will vary the oxides given in Table 4 over the listed ranges of concentrations while holding the remaining ash components at a constant value. The ranges of concentrations and the constant values of the remaining components are based on the ranges and average compositions reported by T. C. Johnson for RFETS incinerator ash.¹

We will perform the variability study using hafnium and neodymium oxides as surrogates for plutonium and americium. These oxides are currently being used for the plutonium vitrification and americium/curium stabilization programs at SRS.

We have performed several scouting experiments to define the processing conditions for the experimental

design. Using the simulated ash composition from the statistically designed experiments with potentially the highest melting point (high refractory and low alkali/alkaline earth concentrations), we successfully formed borosilicate and soda-lime-silicate glasses at 1350°C. We used a 50 wt % ash loading for the soda-lime-silicate glass and an 80 wt % loading for the borosilicate glass. Both glasses poured reasonably well, indicating an acceptable viscosity at 1350°C. Carbon was removed from the ash before vitrification by calcining at 900°C for 2 h. A melt was also performed with the soda-lime-silicate glass formulation using a 2-h hold point at 900°C for carbon removal. Examination of the glass showed a small metal sphere embedded in the center, presumably a copper-nickel alloy seen in previous melts.

The results from the scouting experiments have governed our decision to form the 20 glasses defined by the statistical design at 1350°C using a 2-h hold point at 900°C for carbon removal. At a later date, we will address reduction of transition metals by carbon in the melt. We decided to focus exclusively on the soda-lime-silicate glass formulation because of the simplicity of the glass frit composition (60 wt % silicon dioxide [SiO₂], 30 wt % sodium oxide [Na₂O], and 10 wt % calcium oxide [CaO]). We will use a 50 wt % ash loading for all melts. The response variables for the experiments will include the ease of pouring (a measure of viscosity) and appearance of the

glass (amorphous versus crystalline). To quantify our experimental results, we will probably examine selected glasses by x-ray diffraction, scanning electron microscopy, or other analytical techniques. Once this set of experiments is complete, we will perform additional experiments, using both simulated and actual RFETS ash, to investigate the behavior of plutonium in the soda-lime-silicate glass.

Reference

1. T. C. Johnson, "Recovery of Plutonium from Incinerator Ash at Rocky Flats," Rocky Flats Plant report RFP-2520 (1976).

***Surveillance and Monitoring:
Tomography***

Principal Investigator: Lynn Foster

Task Description. The Surveillance and Monitoring Project aims to develop a noninvasive, nondestructive method for determining (1) the contents of nuclear materials containers and (2) the condition of the transuranic materials stored in these containers. The objective of this project is to eliminate unnecessary and unsafe handling of the containers and their contents.

Status/Accomplishments. This project is in its final stage. Researchers at Los Alamos National Laboratory and Savannah River Site (SRS) are currently collecting data for experimental evaluation of several different tomographic systems. Two tomography phantoms constructed for this project by SRS and Los Alamos have been shipped for tomographic imaging on systems at Lawrence

Livermore National Laboratory and Allied Signal, Inc.

Before shipping, Los Alamos personnel imaged one of the phantoms at Los Alamos radiography facilities using high-energy radiography and medium-energy tomography systems. We are currently analyzing these imaging data.

After completion of the imaging at Livermore and Allied Signal, SRS personnel will image the phantoms on the new tomography system at the SRS radiography facility. Researchers at Los Alamos and SRS will analyze and evaluate all imaging data. In the second quarter of fiscal year 1997, project participants will issue a report describing the capabilities and limitations of tomography for inspection of nuclear materials.

***Surveillance and Monitoring:
Moisture Probe***

Principal Investigator: Lynn Foster

Task Description. This project involves field testing of a neutron-based moisture probe at Los Alamos National Laboratory's Plutonium Facility. Science Applications International Corporation (SAIC) is currently developing a benchtop model moisture detection system for nondestructive analysis of moisture content in plutonium oxide (PuO_2). After SAIC delivers the benchtop model to Los Alamos, Los Alamos researchers will test it using PuO_2 with known moisture content sealed in long-term storage containers. For this study, Los Alamos researchers will produce and characterize PuO_2 standards that bracket the 0.5 wt % maximum moisture content required by DOE-STD-3013 for long-term storage of PuO_2 . Project personnel will then evaluate the applicability of neutron-moderation techniques for quantifying moisture content in PuO_2 at or below the 0.5 wt % level.

Accomplishments/Status. SAIC has performed the Monte Carlo calculations necessary to finalize the design of the benchtop model detection system and to optimize system sensitivity for moisture detection. SAIC has ordered and received the materials for construction of the

benchtop model. SAIC is now constructing the benchtop model and preparing a laboratory for benchtop model testing. Benchtop model testing at SAIC will use surrogate materials to represent the PuO_2 . SAIC researchers selected surrogate materials that will match the neutronic absorption and scattering properties of PuO_2 . Small-diameter polymer rods will simulate the moisture content by matching the hydrogen atom density in the surrogate material. With the goal of improving system performance, SAIC will feed information from its benchtop model testing back into the design process.

Los Alamos researchers have begun producing standards for the moisture probe field tests. These standards will have loss on ignition ranging from 0.1 to 1.0 wt % moisture to bracket the long-term storage requirement of 0.5 wt % moisture. The standards, which will be packaged in the same configuration currently used in the oxide repackaging effort, will be characterized for major contaminants and moisture content by destructive analysis. These standards will serve as a tool to evaluate the performance of the benchtop model moisture detection system at Los Alamos.

***Surveillance and Monitoring:
Acoustic Resonance Spectroscopy***

Principal Investigator: D. Kirk Veirs

Task Description. The objective of the Acoustic Resonance Spectroscopy Project is to develop a noninvasive, nondestructive method for monitoring increases in gas pressure and changes in gas composition within sealed storage containers. The method is based on using acoustical excitation and detection to measure the properties of standing waves produced in a gas contained within an acoustic cavity. The frequency of the standing waves changes with gas composition, and the intensity changes with gas pressure.

Status/Accomplishments. During the first quarter of fiscal year 1997, Los Alamos National Laboratory researchers constructed an analytical working curve that relates observed frequencies to an effective average mass of the gas. The researchers also investigated a mathematical approach to fitting observed acoustical resonance data in order to obtain line positions, linewidths, and intensity.

Analytical Working Curve. In the previous status report for the 94-1 Research and Development Project,¹ we showed that for a cylindrical cavity, all observed gas resonance frequencies can be predicted from the geometry of the cavity and the velocity of sound of the gas:

$$v = \frac{c}{2} \cdot \frac{1}{\sqrt{\left(\frac{n_z}{l}\right)^2 + \left(\frac{\alpha_{n,m}}{a}\right)^2}} \quad (1)$$

The velocity of sound for an ideal gas is related to the average molar mass of the gas by

$$c^2 = \frac{\gamma \cdot RT}{\langle M \rangle} = \frac{\langle Cp \rangle}{\langle Cv \rangle} \cdot \frac{RT}{\langle M \rangle}, \quad (2)$$

where $\langle \rangle$ signifies the ensemble average. For a gas mixture containing only monatomic gases, this equation can be written as

$$c^2 = \frac{5}{3} \frac{RT}{M_{\text{eff}}} \quad (3)$$

The effective mass, M_{eff} , is related to the actual average mass of the gas by

$$\langle M \rangle = (1 - \delta) M_{\text{eff}} \quad (4)$$

where δ is a correction factor that arises because the heat capacity of the actual gas mixture is different from that for an ideal gas mixture:

$$\delta = \frac{\frac{2}{5} \cdot \frac{\langle Cp \rangle}{R} - 1}{\frac{\langle Cp \rangle}{R} - 1} \quad (5)$$

We can calculate an analytical working curve for the cylindrical cavity described in the previous status report.¹ The height of the cylinder, l , is 1 inch, determined with Eq. 3 and Eq. 1. The working curve shown in

Fig. 3 plots M_{eff} as a function of frequency. The working curve allows us to obtain the effective mass of the gas immediately from the observed frequency. We have calculated M_{eff} at room temperature for a number of gases. (See Fig. 3.)

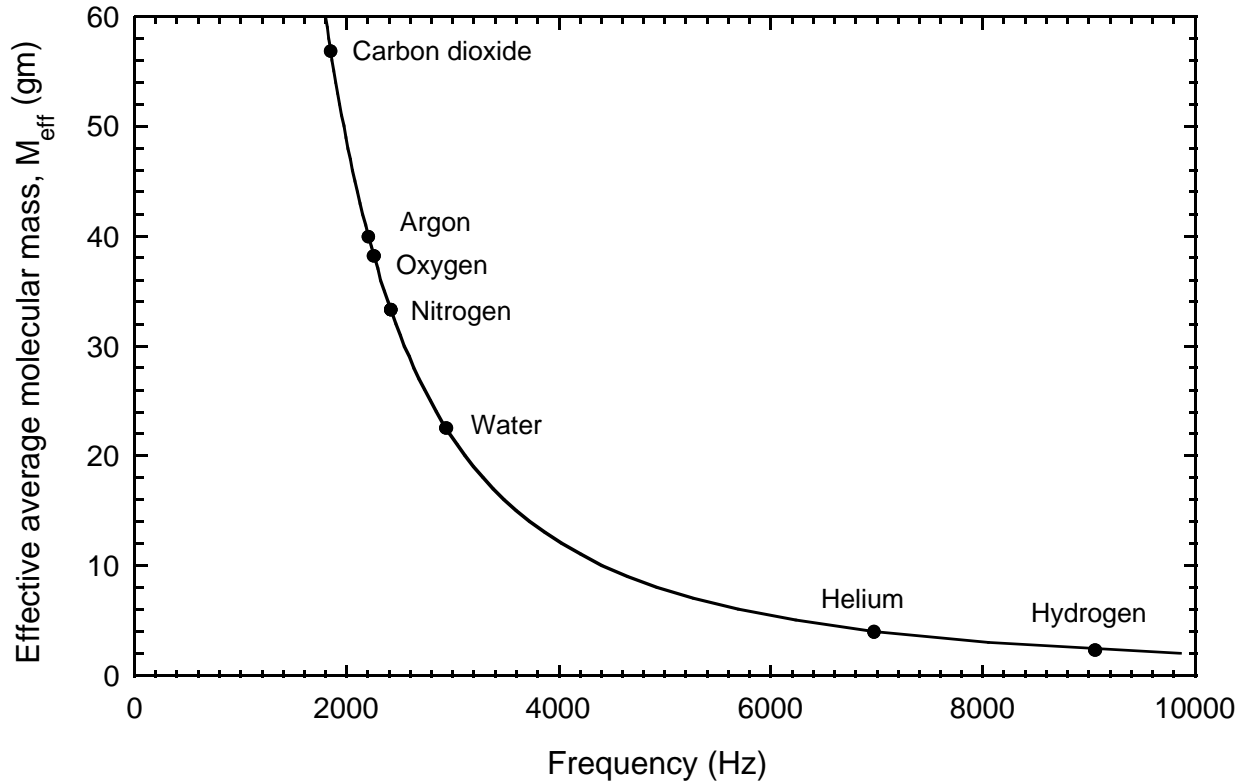


Fig. 3. Analytical working curve for a 1-in. cylindrical cavity.

Mathematical Fitting of Observed Data. We have mathematically modeled acoustic resonance data of gas mixtures using a background term with phase and a Lorentzian line shape with phase for each observed container and gas resonance. Using this approach, we obtain an excellent fit, reproducing all aspects of the observed resonances as shown in Fig. 4. The initial decrease in the signal

arises because the gas mode and the background are out of phase. As the frequency passes through the center frequency of the gas mode, the phase of the gas mode shifts by 180 degrees; the gas mode and the background are now in phase, resulting in an increased signal. The small mode at 2440 Hz is due to the container. Using this mathematical approach to fitting data, we can accurately obtain the gas mode frequency and linewidth.

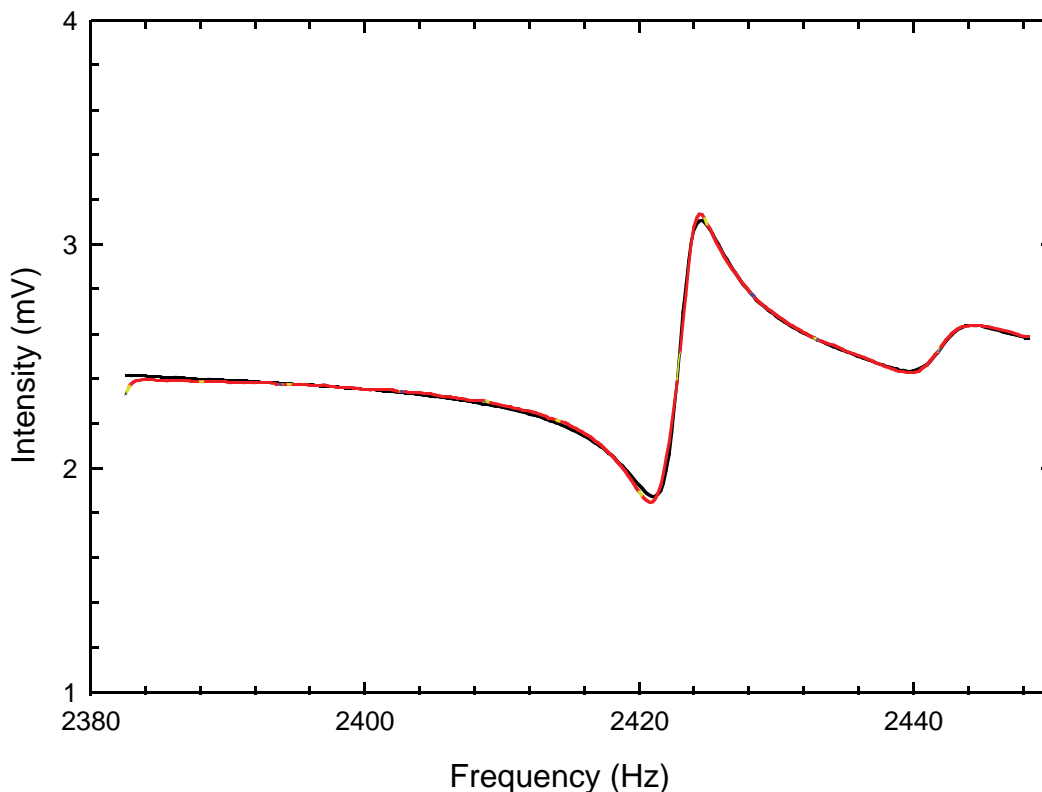


Fig. 4. The acoustic resonance of a gas mixture containing helium, nitrogen, and carbon dioxide gas. The data and a fit to the data are shown.

Experimental Setup. We are designing and fabricating a new experimental setup that will allow us to mix gases with precise control of their composition. This new capability will allow more accurate study of the effect of gas composition on linewidths and line positions. The design of the inner storage container to be used at Los Alamos has been refined. We will obtain a storage container with the new design, fit the container with a cylindrical cavity, and test the container with a variety of gas mixtures. We will investigate the

ability to observe and quantitatively interpret gas modes with this new container design.

Reference

1. D. Kirk Veirs and Clinton Heiple, "Surveillance: Acoustic Resonance Spectroscopy," in "94-1 Research and Development Project Lead Laboratory Support: Status Report July 1–September 30, 1996," Nora Rink, Comp., Los Alamos National Laboratory report LA-13231-SR (March 1997), pp. 44–50.

***Surveillance and Monitoring:
Nondestructive Assay—Gamma Salts***

Principal Investigator: Teresa Cremers

Task Description. This project provides a means to analyze heterogeneous plutonium- and americium-bearing salts for plutonium isotopic distribution and americium concentration.

Status/Accomplishments. During the first quarter of fiscal year 1997, Los Alamos National Laboratory researchers collated and assembled spectra from various plutonium-

bearing salts. We examined about 150 spectra from about 20 separate items. We developed and tested preliminary parameter sets for the gamma-ray isotopic distribution of plutonium salts with high americium concentration (greater than 10 000 parts per million [ppm]). Initial results are promising, and during the second quarter of fiscal year 1997, we expect to fine-tune our analyses.

***Surveillance and Monitoring:
Calorimetry***

Principal Investigator: Teresa Cremers

Task Description. This project applies finite element analysis to obtain a model that will predict calorimeter performance and permit the design of smaller, faster calorimeters.

Status/Accomplishments. Los Alamos National Laboratory experimenters from the Engineering Analysis Group in the Engineering Sciences and Applications Division (ESA) and from the Safeguards Science and Technology Group are supporting this project. We are using the ABAQUS computer code and will also apply a

highly integrated design tool, IDEAS, which supports flexible mesh generation and some thermal modeling. Our intent is to use IDEAS for the mesh generation and to use ABAQUS for the thermal modeling. A graduate student in ESA is using these tools to work on an adiabatic calorimeter model. We are discussing plans with researchers at the University of Dayton Research Institute for them to run additional configurations through their existing model.

***Surveillance and Monitoring:
Risk Status of Residue Holdings at Rocky Flats Environmental Technology Site***

Principal Investigator: Tom Rising

Task Description. The objective of this project is to assess the risk status of Rocky Flats Environmental Technology Site (RFETS) residue holdings described in the Defense Nuclear Facilities Safety Board's (DNFSB's) Recommendation 94-1. At issue is the change in risk status during the past 3 years that resulted from aging effects and from mitigation efforts, such as drum venting and repackaging. The assessment will address the risk status before DNFSB 94-1 remediation efforts and the current risk status. The analysis will also provide information essential to development of methodologies for predicting future risk behavior based on various program scenarios.

Status/Accomplishments. A team from the Los Alamos National Laboratory Technology Modeling and Analysis Group went to RFETS and interviewed various knowledgeable Department of Energy and Kaiser-Hill Company personnel. These meetings confirmed the scope, schedule, and

intended application of the project. The project is planned for completion before May 1997, which is the third anniversary of the DNFSB Recommendation 94-1; this is the target date for stabilization of all high-hazard materials. In addition to developing plans for stabilizing residues, RFETS personnel have taken many steps to address high-risk situations. A major thrust of this project is to develop an objective measure of the effectiveness of stabilizing actions.

The team also collected data from RFETS and interviewed several RFETS subject matter experts to better understand the data and the risks associated with the residue holdings.

Los Alamos researchers are planning a risk workshop to be conducted for DOE. The workshop will be scheduled when workshop parameters such as date, location, scope and content, participants, attendees, format, and agenda are formalized.

Core Technology:

Actinide Solution Chemistry in Residues and in Residue Stabilization and Treatment Processes

Principal Investigator: John M. Berg

Task Description. Los Alamos National Laboratory researchers seek to describe aspects of the solution chemistry of actinide elements in legacy residues and in proposed residue treatment processes. Information on solution chemistry is useful to guide stabilization and disposition decisions and to enable efficient optimization of residue treatment processes.

Status/Accomplishments. Sample preparation, data acquisition, and data analysis on both the Pu(IV) nitrate acid system and the Pu(VI) chloride near-neutral system all progressed substantially during the first quarter of fiscal year 1997 (FY97).

We are currently analyzing data contained in spectra of 700 plutonium

nitrate solution samples to obtain thermodynamic constants for those complexes at 10 ionic strengths. Concurrently, we have continued experiments investigating the effects of other dissolved salts on the nitrate system.

Experimental work in the first quarter of FY97 focused on chloride complexation of Pu(IV). Our initial results suggest formation of both outer-sphere and inner-sphere chloride complexes. Thus far, nitrate data analysis has shown that the formation complexes for low plutonium nitrate complexes increase by up to an order of magnitude when the ionic strength increases from 2 M to 17 M. Fig. 5 shows the spectroscopic changes in one wavelength region over that range of conditions.

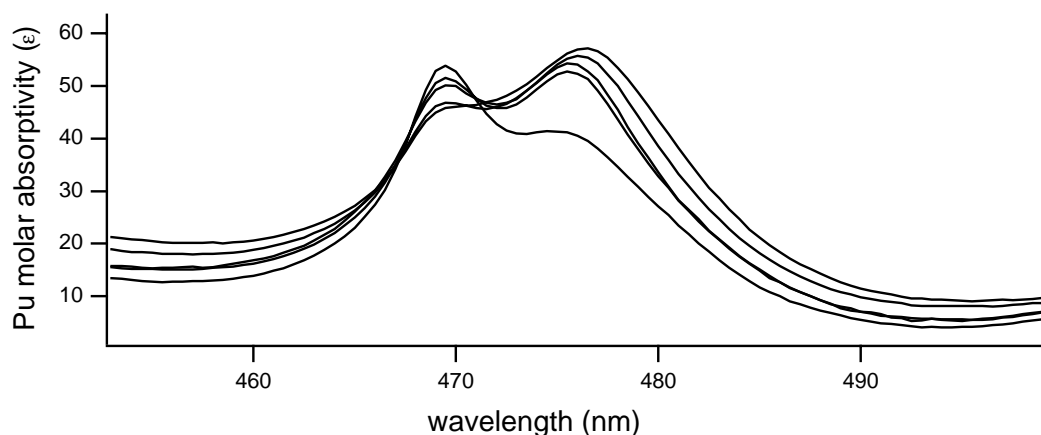


Fig. 5. The effect of ionic strength (I) on speciation of Pu(IV) nitrate complexes is illustrated by significant shifts in absorption spectra of Pu(IV) at constant nitrate concentration but increasing I.

Core Technology:

Chemical and Physical Interactions of Actinides with Residue Substrates

Principal Investigator: David Morris

Task Description. This project focuses on molecular spectroscopic characterization of the interaction of plutonium and other actinides with several classes of important residues, including combustibles (ion-exchange resins and cellulosic materials) and incinerator ash.

Status/Accomplishments. In the first quarter of fiscal year 1997 (FY97), Los Alamos National Laboratory researchers focused experimental efforts on investigations of the nitric acid degradation of anion-exchange resins. In particular, we initiated studies on a second class of resin commonly used in plutonium processing, Reillex HPQ™. We are nearing completion of these degradation studies and will proceed to study the exchange chemistry of these degraded materials in the second quarter of FY97.

During the first quarter of FY97, we made significant progress on the spectroscopic characterization of the effects of accelerated aging (by elevated temperature) and concentrated nitric acid on the degradation of anion-exchange resins. Most notably, we began experiments on a second important and relevant class of resins, namely the pyridinium-based anion exchanger Reillex HPQ. We chose this material because it has received significant use in plutonium processing and

it provides a comparison with the material used in our ongoing investigations, Dowex-11™, which is a more classical quaternary ammonium-based material. Our focus has been on vibrational and luminescence spectroscopic probes of changes in either the backbone or the active exchange sites in these materials, with particular emphasis on indications of nitration of the organic moieties in these materials that could lead to potentially explosive compounds. During this period, we also added Fourier-transform Raman spectroscopy to our repertoire for resin characterization.

Our experiments with Dowex-11 and Reillex HPQ have been done as a function of nitric acid concentrations ranging from 0 to 12 M (i.e., spanning the range of plutonium processing relevance) and temperatures ranging from room temperature to about 60°C. Most recently, we have taken the resins resulting from these reactions and fully exchanged them with Cl⁻ to remove excess nitrate from the anion-exchange sites, thus enabling us to look in greater detail for incorporation of nitrate into the resin structure. Our results to date, although not yet fully analyzed, indicate that there are spectroscopic changes consistent with resin degradation under these reactive

conditions. We have not yet completed the analysis necessary to make conclusions regarding nitration.

Our next course of action is to prepare batch lots of these degraded resins for use in exchange reactions with plutonium under comparable chemical conditions. These studies will allow us to determine if the degraded materials provide new, perhaps more reactive, sites for interaction with the plutonium species that exist under high-nitric-acid processing conditions.

Our summer undergraduate student, Mr. Aaron Wheeler of Furman University, presented a talk titled “Interactions of Uranium with Environmental and Waste Form Matrices” at the 1996 Southeast Regional American Chemical Society Meeting, held November 10–13, 1996, at Greenville, South Carolina. Mr. Wheeler was also nominated and made the short interview list for a Rhodes Scholarship in his home state of Georgia. Regrettably, he was not one of the final two nominees to go forward in national competition.

Core Technology:

Identification and Characterization of Changes in the Chemical State of Plutonium in Interim Waste Forms

Principal Investigator: D. Kirk Veirs

Task Description. The purpose of this work is to identify and characterize changes in the physicochemical state of the myriad plutonium compounds found in residues. For plutonium-containing materials other than metal and pure oxide, techniques such as powder and single-crystal x-ray diffraction (XRD), x-ray absorption spectroscopy (XAS), x-ray photoelectron spectroscopy (XPS), and optical spectroscopies (reflectance absorption and Raman) will identify changes in the local chemical environment of the plutonium metal center. Changes in the local chemical environment can indicate the onset of deleterious transformations in the waste form that may lead to unsafe storage conditions.

Status/Accomplishments. During the first quarter of fiscal year 1997, Los Alamos National Laboratory researchers prepared samples for the January 1997 experimental run at Stanford Synchrotron Radiation Laboratory (SSRL). These samples include a plutonium metal standard for calibrating the x-ray absorption near-edge structure (XANES) data and a residue sample of spent ion-exchange resin that had been stored for many years in a steel canister. We determined the XANES edges of ten $\text{Pu}(\text{NO}_3)_6^{2-}$ samples and compared

them with the XANES edges of the $\text{Pu}(\text{IV})$ aquo species reported earlier.¹ The substitution of nitrate ligands for the hydrating waters produced no discernible change in the XANES edge energy.

Sample Preparation. Determining the oxidation state of plutonium by precisely measuring the energy of the XANES edge requires a set of well-characterized calibration samples. We have published the XANES edge energies for plutonium aquo species in oxidation states III, IV, V, and VI in the previous quarterly status report.² We found a linear relationship between the XANES edge energy and the oxidation state for these aquo species. To complete our calibrations, we must determine XANES edge energies for plutonium species complexed with ligands and in other chemical states (such as pure solids, complex powders or slurries, etc.) expected to be common in residues.

We are preparing a set of carbonate species for the June 1997 experimental run at SSRL. This set includes samples with plutonium in the III, IV, V, and VI oxidation states. We have prepared solid samples for XRD experiments and have characterized these samples by ultraviolet-visible absorption spectrum/near infrared (UV-VIS/NIR) absorption spectroscopy.

The plutonium XANES edge spectra are calibrated using a zirconium foil. The XANES edge for the zirconium foil lies 50–60 eV lower in energy than the plutonium XANES edge does. A separate scan is required to record the zirconium spectrum. We have obtained a plutonium metal sample, made of a plutonium alloy that is resistant to oxidation, for use as a calibration standard. We have fabricated a sample holder (primary, secondary, and tertiary containment) and we will test the sample during the June SSRL run. During the run, the plutonium secondary standard will be calibrated against the zirconium primary standard. The XANES spectrum of the plutonium calibration standard will be collected at the same time plutonium sample data are taken.

We have obtained a sample of spent ion-exchange resin for XANES and extended x-ray absorption fine-structure (EXAFS) characterization. The sample has been stored in the Los Alamos National Laboratory Plutonium Facility vault for 4 years. The sample has reacted with the storage vessel, and substantial chemical changes have taken place. The steel inner can has been completely corroded, and the sample contains large amounts of iron-containing corrosion products. The oxidation state and chemical composition of the plutonium compounds now existing in the sample are unknown. The XANES spectra will be used to obtain information concerning the oxidation state. We plan to compare the EXAFS spectra of this sample with EXAFS

spectra of plutonium nitrate species from previous work.

XANES Edge of Plutonium

Hexanitrate Species. In previous work, we determined the XANES edge energy for plutonium aquo species as a function of oxidation state.¹ The calibration curve derived from this previous work might be used to determine plutonium oxidation states in samples for which the oxidation state is unknown. For the technique to be universally useful, we need to fully understand the effect of complexing ligands and chemical forms on the plutonium XANES edge energies.

We have analyzed XANES data from ten samples of carefully prepared $\text{Pu}(\text{NO}_3)_6^{2-}$ to obtain the XANES edge energy (the plutonium is in the IV oxidation state). We prepared the samples by sorbing Pu^{4+} onto anion-exchange resins from 7 M nitric acid. The characterization of plutonium species sorbed onto anion-exchange resins from nitric acid has been studied for several decades, and the only plutonium species detected is $\text{Pu}(\text{NO}_3)_6^{2-}$. The six nitrate ligands are bidentate, resulting in a plutonium ion with a coordination number of 12.

The plutonium species we used to determine the XANES edge energy calibration curve was completely coordinated with water; however, how many waters are associated with the plutonium in the $\text{Pu}(\text{IV})$ aquo species is unknown. Previous EXAFS work suggests that the coordination number may be as high as 10 or 11.³

Replacing the waters with nitrates results in a substantial change in the electronic structure of the Pu(IV) ion, as indicated by dramatic changes in the UV-VIS/NIR spectra. Thus, comparing the $\text{Pu}(\text{NO}_3)_6^{2-}$ species XANES edge energy with the Pu(IV) XANES edge energy from the calibration curve will be a good test of the effect of speciation on the XANES edge energy.

We analyzed two spectra from each of the ten samples using the approach reported previously.² We used an arc tangent and two Gaussians to fit the data and reported the position of the arc tangent as the XANES edge energy. The spectra were calibrated using the inflection point of the zirconium spectra. The result from the 20 data sets is a XANES edge energy of $18\,057.67 \pm 0.34$ eV (2 sigma). The XANES edge energy result for Pu(IV) from the calibration curve reported previously¹ is 18 057.6 eV. The results are in excellent agreement and suggest that speciation may not shift the XANES edge energy.

References

1. S. D. Conradson, I. A. Mahamid, D. L. Clark, N. J. Hess, et al., "X-Ray Absorption Edges of Plutonium in Different Oxidation States," (submitted to *Polyhedron*).
2. D. Kirk Veirs and Mary Neu, "Core Technology: Changes in the Chemical State of Plutonium," in "94-1 Research and Development Project Lead Laboratory Support: Status Report July 1–September 30, 1996," Nora Rink, Comp., Los Alamos National Laboratory report LA-13231-SR (March 1997), pp. 59–64.
3. P. G. Allen, D. K. Veirs, S. D. Conradson, C. A. Smith, and S. F. Marsh, "Characterization of Aqueous Plutonium(IV) Nitrate Complexes by Extended X-ray Absorption Fine Structure Spectroscopy," *Inorg. Chem.* **35**, 2841–2845 (1996).

***Core Technology:
Actinide-Organic Interactions***

Principal Investigators: Carol J. Burns and Steven D. McKee

Task Description. This study examines the interaction of plutonium and other actinides with organic substrates. Research is conducted on (1) interactions between actinide residues and organic substrates and (2) actinide organometallic chemistry.

Status/Accomplishments. Facilities modification efforts at Los Alamos National Laboratory's Plutonium Facility (TA-55) continued during the first quarter of fiscal year 1997 (FY97). These efforts were impacted by a TA-55 building PF-4 stand-down.

During the first quarter of FY97, Los Alamos National Laboratory researchers initiated experiments to characterize the surfaces of chosen matrices and study the aqueous uptake of actinides on these matrices.

Facilities Modification. Initial machining inaccuracies required rescheduling work related to the retrofit of our glovebox optics well, and so this task has not been completed. Additional work to be completed includes polishing the weld, a Johnson Controls World Services, Inc. crafts job, and well placement, which is to be accomplished by project personnel. A planned glovebox window change has been deferred. When retrofit activities are completed, we will purge the glovebox with helium and regenerate

the catalyst bed. We will then operate the glovebox for a period to evaluate the atmosphere and assess readiness for routine operation. At that time, the group level readiness assessment (GLRA) will be conducted. In preparation for the GLRA, we have written additional experimental plans to address waste handling and the use of cryogenic fluids (i.e., liquid nitrogen).

Aqueous Actinide-Organic Interactions. As discussed in the previous quarterly status report,¹ the Los Alamos National Laboratory project team has chosen the following as representative organic materials to study as surrogate matrices

- plastics, such as polystyrene, Kynar™, and polyethylene/polypropylene, and
- cellulosic materials representative of filters, rags, etc.

We have been working with the surface characterization project team at Los Alamos to identify an initial set of substrates common to both projects. We can then coordinate our chemical functionalization tasks with the surface characterization studies already planned, thereby generating a more complete picture of chemistry associated with matrix degradation, whether chemical or radiolytic. The

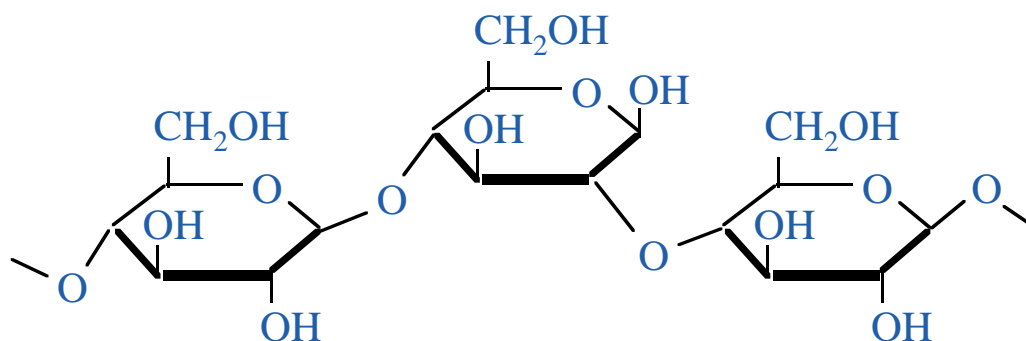


Fig. 6. Chemical structure of cellulose.

initial substrate chosen for study is cellulose (Fig. 6); a fibrous form of material (Whatman CF-1™) will be employed in initial solution uptake studies.

We have designed an experimental plan to correlate plutonium uptake information with uranyl uptake information obtained in the surface characterization project. In order to take advantage of transuranic handling capabilities and experimental facilities, we will conduct these experiments at Los Alamos National Laboratory's Radiochemistry Site during the building PF-4 stand-down.

We will be procuring technical assistance from Los Alamos National Laboratory's Nuclear and Radiochemistry Group to initiate the experiments. We will use redox-pure aqueous solutions of plutonium in chloride media for the direct aqueous contacting experiments. While it is acknowledged that the solution matrix (either nitrate or chloride) will likely have an effect on the observed chemistry, we will conduct initial studies in chloride solution in order to minimize the risk of organic nitration. Solution variables to be mapped out in

the study include plutonium oxidation state (+3/+4), metal ion concentration, solution pH (within accessible ranges precluding precipitation), and contacting time. Source plutonium and matrix material have been identified, and the studies should commence early in January 1997.

We anticipate that little native uptake of actinide will occur in the unfunctionalized cellulose. The principal functional group capable of metal ion complexation is the hydroxyl group; this ligation is expected to be weak at low solution pH. However, these studies will serve as baseline data with which to compare further studies in which the cellulose has been chemically or radiolytically treated. These studies will also serve to establish the experimental protocol. Any substrates which do show evidence of plutonium binding will be sent to the surface characterization team for evaluation of surface chemical interactions.

We have initiated literature studies to determine the appropriate experimental parameters to employ to effect selective functionalization of the cellulose substrates. Ultimately, acid

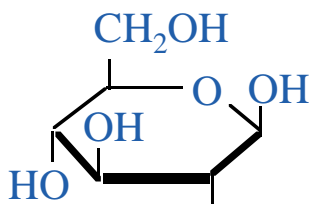


Fig. 7. Glucose.

hydrolysis results in complete degradation to the monomer D-glucose (Fig. 7). Solution studies will commence in the third quarter of FY97 to investigate the solution chemistry of the monomer with plutonium.

Other means of functionalization may be feasible, however, including partial hydrolysis or radiolysis to oligosaccharides, limited nitration, esterification, and oxidation of the alcohol functional groups pendent on

the saccharide rings. Once matrix treatment reactions have been chosen, we will completely characterize the degraded/functionalized substrates for repeat uptake experiments. In addition, we will study the rates of these functionalization reactions both in the presence and absence of plutonium ions to examine the impact of metal on organic reactivity.

Reference

1. Carol Burns and Steven McKee, "Core Technology: Actinide-Organic Interactions," in "94-1 Research and Development Project Lead Laboratory Support: Status Report July 1–September 30, 1996," Nora Rink, Comp., Los Alamos National Laboratory report LA-13231-SR (March 1997), pp. 65–66.

Core Technology:
Corrosion

Principal Investigator: Darryl P. Butt

Task Description. The corrosion project incorporates two different tasks. The primary thrust is to examine the effects of crystallographic orientation on the electrochemical behavior of engineering materials by coupling localized corrosion measurements with orientation imaging microscopy. The second portion of the corrosion effort is to examine the effects of crystallographic texture on stress corrosion cracking of materials.

Status/Accomplishments.

Examination of the effect of texture on localized corrosion is under way. The first part of this research involves design and production of three items critical to this research but not commercially available: (1) material having specific textures, (2) scanning reference electrode probes, and (3) an electrochemical cell. To date, we have done preliminary studies of the effects of texture on the corrosion of stainless steel, nickel, and beryllium. In all three cases, we have observed significant textural effects. Work is now aimed at examining these effects in a more systematic way. Current studies are

focused on commercially pure nickel (^{270}Ni). We have subjected ^{270}Ni powder to hot isostatic pressing (HIP) to produce material with an approximately random orientation. We will subsequently roll a portion of this material to obtain material with a strong texture. Then we will anneal a portion of the rolled material to obtain material with a texture different from the as-HIPed and the rolled material. The materials of different texture are scheduled for production in early 1997. We are fabricating ^{270}Ni single crystals for comparison.

We have designed scanning reference electrodes, which are currently in production. These electrodes consist of two very fine (15- μm diameter) platinum wires disposed 50 μm apart and separated by insulating material. Production of the electrodes is nontrivial, as the probe dimensions are of a very fine scale. We designed a method for the production of these probes during the first quarter of fiscal year 1997 (FY97), and delivery should occur early in the second quarter. The design for these electrodes is displayed in Fig. 8.

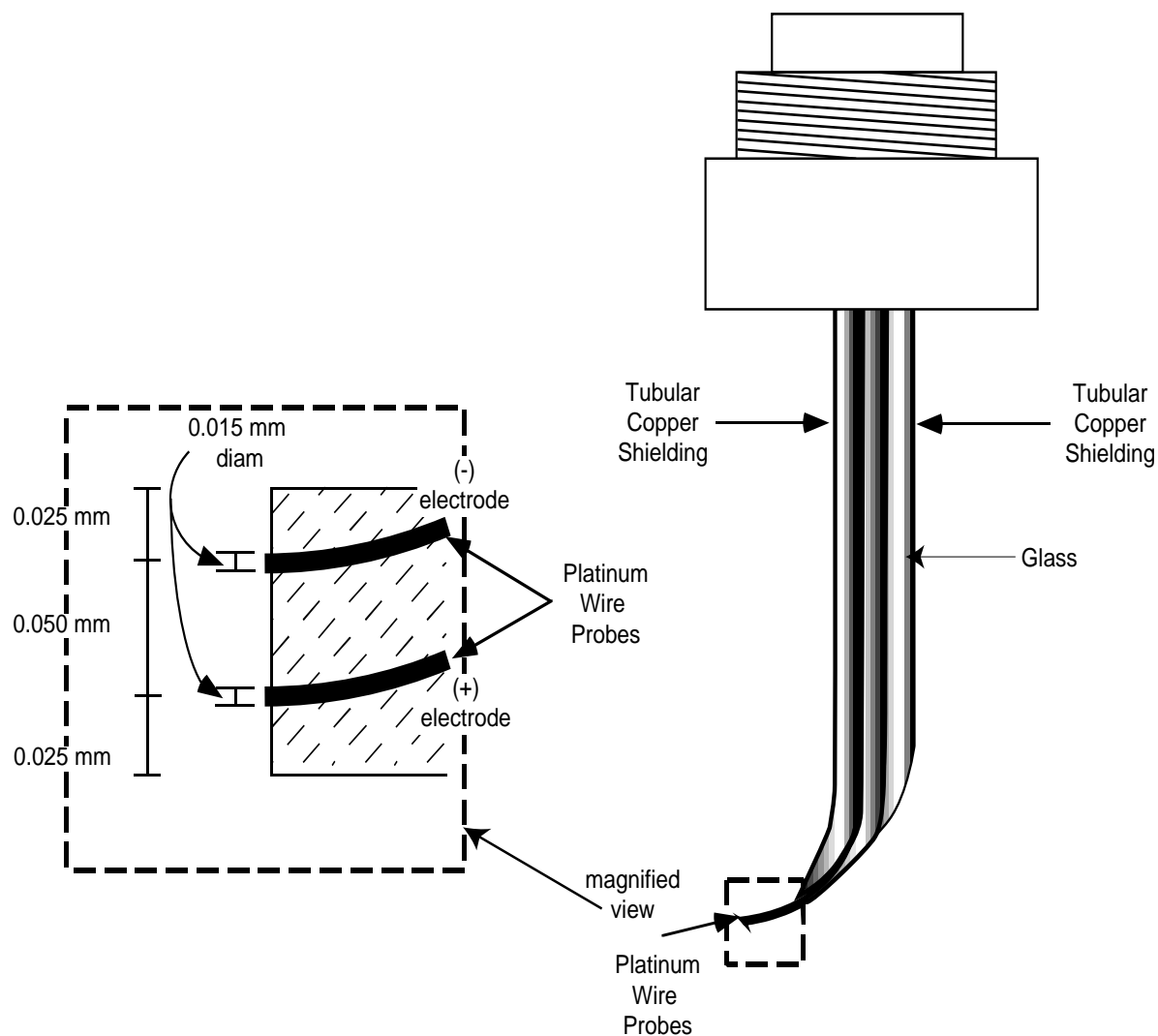


Fig. 8. Scanning reference electrode probe design.

During the first quarter of FY97, we designed and built a special electrochemical cell for scanning reference electrode testing. This cell incorporates (1) releasable mounting of a sample with prevention of solution egress, (2) translation in three dimensions, and (3) rotation about two axes. The cell also allows a sample to be positioned in space with the sample surface maintained parallel to the plane of travel of the reference probe.

Setup and fabrication of the stress corrosion cracking apparatus is ongoing. We procured two mechanical test frames from Rocky Flats Environmental Technology Site. We have upgraded a vertical load frame, which is now operable. A horizontal frame is ready for upgrade and should be functional by the end of January 1997. Work in the second quarter of FY97 will involve design and production of an electrochemical cell and samples.

***Core Technology:
Plutonium Diffusion Science***

Principal Investigator: Pamela K. Benicewicz

Task Description. The objective of the Plutonium Diffusion Science Project is to measure and understand room-temperature, long-term diffusion of plutonium into materials such as stainless steel. Meeting this objective will require experimental measurements of diffusion coefficients near room temperature. Diffusion coefficients for plutonium have been measured at high temperatures for some materials. These diffusion coefficients are highly dependent upon temperature and concentration. These measured diffusion coefficients have been extrapolated to the lower temperatures relevant to long-term storage. This project involves the experimental verification of these extrapolations.

Status/Accomplishments. Researchers at Los Alamos National Laboratory have collected samples of plutonium diffusion systems and cut them into 1-in. coupons. These samples, which are approximately 30 years old, include plutonium diffused into stainless steel, uranium, and beryllium. During the first quarter of fiscal year 1997, we have spent time

converting part of Los Alamos National Laboratory's Technical Area 46 (TA-46) into a radiological controlled area. Upon completion, personnel at TA-46 will be able to accept samples and, using the secondary ion mass spectroscopy apparatus at TA-46, perform depth profile analyses to determine plutonium diffusion depth.

We purchased a beam profile analyzer to view the output of the neodymium-doped yttrium-aluminum-garnet (Nd:YAG) laser located at the Los Alamos Plutonium Facility's building PF-42. The output is specified to have a Gaussian profile. Unfortunately, our laser output is showing diffraction rings rather than the expected Gaussian intensity profile. We are currently working with the manufacturer to determine the source of the problem. Our ultimate goal is to convert the Gaussian output to a flat-top profile to improve resolution for profiling studies. (Only one layer is sampled with a flat-top beam, whereas multiple layers are sampled with a Gaussian beam.)

Core Technology:
Separations—Polymer Filtration

Principal Investigators: Gordon D. Jarvinen and Barbara F. Smith

Task Description. The polymer filtration process removes actinides to very low levels from solutions produced by stabilization operations. This process is performed in order to meet site-specific liquid discharge requirements. The objective of this project is to optimize the polymer filtration process.

Status/Accomplishments

Polymer Characterization. During the first quarter of fiscal year 1997 (FY97), Los Alamos National Laboratory researchers have made progress in gel permeation chromatography, the polymer sizing component of the research. We have acquired and checked out the appropriate equipment (pump, reagent delivery system, column, detector, etc.). We have performed a data acquisition upgrade, and analytical methods are currently being developed.

Additionally, we used one of the diphosphonic acid model compounds in a screening study to evaluate the capability of several chelating agents to remove plutonium and americium from Johnson Atoll soil. This soil was contaminated with plutonium during the era of atmospheric testing of nuclear weapons. While none of the eight reagent combinations tested showed more than 25% removal in one contact, this very preliminary work

showed the diphosphonic acid solution to be the second most effective reagent.

Direct Probing Techniques. In development of direct probing techniques, we are now focusing efforts entirely on laser-induced luminescence. In the first quarter of FY97, we acquired both commercially available and synthetically prepared ligands to serve as model compounds for this fluorescence approach toward characterizing our water-soluble polymers. Methylene diphosphonic acid and 1-hydroxyethylidene-1,1-diphosphonic acid are among those compounds purchased. Dimethylaminomethylene diphosphonic acid and aminoethylene diphosphonic acid are among those compounds synthetically prepared within our laboratory. We have characterized all of these compounds in terms of (1) appearance and (2) solubility in various solvents. We have also characterized these compounds by ^1H , ^{31}P , and ^{13}C nuclear magnetic resonance. We are currently preparing lanthanide salts of these compounds that are similar to the complexes formed between the water-soluble chelating polymers and trivalent americium. We prepared solid metal complexes by combining the diphosphonic acid compounds with lanthanide salts in aqueous solution at various mole ratios and pH values.

Characterization of these solids is proceeding by a variety of methods.

During the first quarter of FY97, we performed actual fluorescence studies (time-resolved and solid-state) on purchased europium salts. These studies confirmed instrument

operation and served as an initial performance check of the experimental system. The system has been modified from its original configuration to accommodate liquid samples in addition to solid substrates. Representative data from these experiments are shown in Fig. 9.

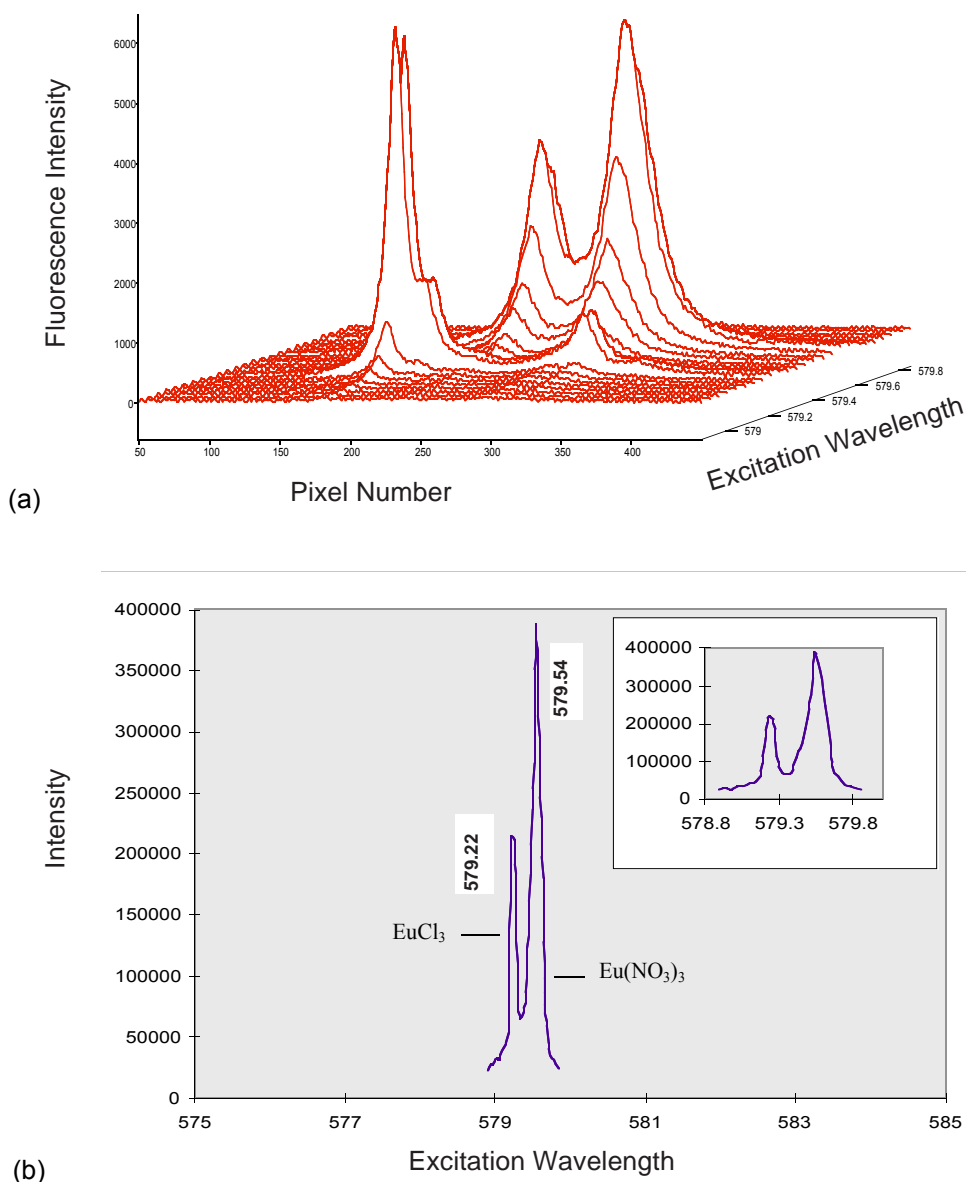


Fig. 9. Lanthanide ion probe spectroscopy (LIPS) analysis of a europium chloride/nitrate mixture. (a) Fluorescence emission spectrum of the monitored 5D_0 - 7F_2 Eu^{3+} transition for a europium chloride/nitrate mixture. (b) Resulting fluorescence excitation spectrum of the 7F_0 - 5D_0 Eu^{3+} transition. The two peaks represent different Eu^{3+} environments.

Core Technology:
Separations—Polymer Foams

Principal Investigators: Gordon D. Jarvinen and Betty S. Jorgensen

Task Description. Los Alamos National Laboratory researchers are investigating polymer foams for use in recovery of radioactive species from waste streams. We are investigating metal uptake on foams with graft-polymerized ligands in comparison with resin beads.

Status/Accomplishments. Our metal uptake studies have shown that foams with graft-polymerized polyvinylpyridine have faster kinetics than resin beads (Reillex™ 425) do. We also performed studies on a polyvinylpyridine/polyvinylphosphonate ester grafted foam. We anticipated that the foams would show faster kinetics than beads do because of the open cellular structure and the flexibility of the grafted chains, and this has proved to be true. In addition, graft-polymerized ligands, such as polyvinylpyridine, appear to provide a new technique to explore the effect of the number of metal binding sites, the ligand chain length, copolymerized ligands, and related phenomena.

We investigated uptake of Fe(III) from 10-N hydrogen chloride (HCl). To approximate similar diffusion times for foam and resin beads, we broke the foam into pieces approximating bead sizes. Metal uptake kinetics in a large piece of foam used in a batch test will be largely dependent on diffusion

rates into the foam. In a column experiment, the diffusion time will be largely eliminated by the flowing solution going through the foam and exposing all surfaces in the foam.

The results of the metal uptake studies are shown in Fig. 10. In that figure, the distribution coefficient is plotted as a function of time. The most notable results are that (1) the kinetics and the distribution coefficient increase with lower degrees of grafting and (2) in all cases, the foams have higher uptake kinetics than do resin beads. This increase in kinetics is particularly notable in cases of shorter exposure times. The foam with the copolymerization of a vinylphosphonate ester showed the highest distribution coefficient.

We selected for functionalization the foams that showed the best flow and structural properties. Foams with a 75/25 ratio of chloromethylstyrene to styrene were treated with thiosulfate. The chloro group is thus replaced with a sulfur-sulfur group that is a free-radical polymerization initiator in the presence of ultraviolet (UV) light. An excess of vinylpyridine is added, and then the foams are exposed to UV light for varying lengths of time. We performed several experiments to determine the degree of grafting obtained with various exposure times. Grafting amounts from approximately

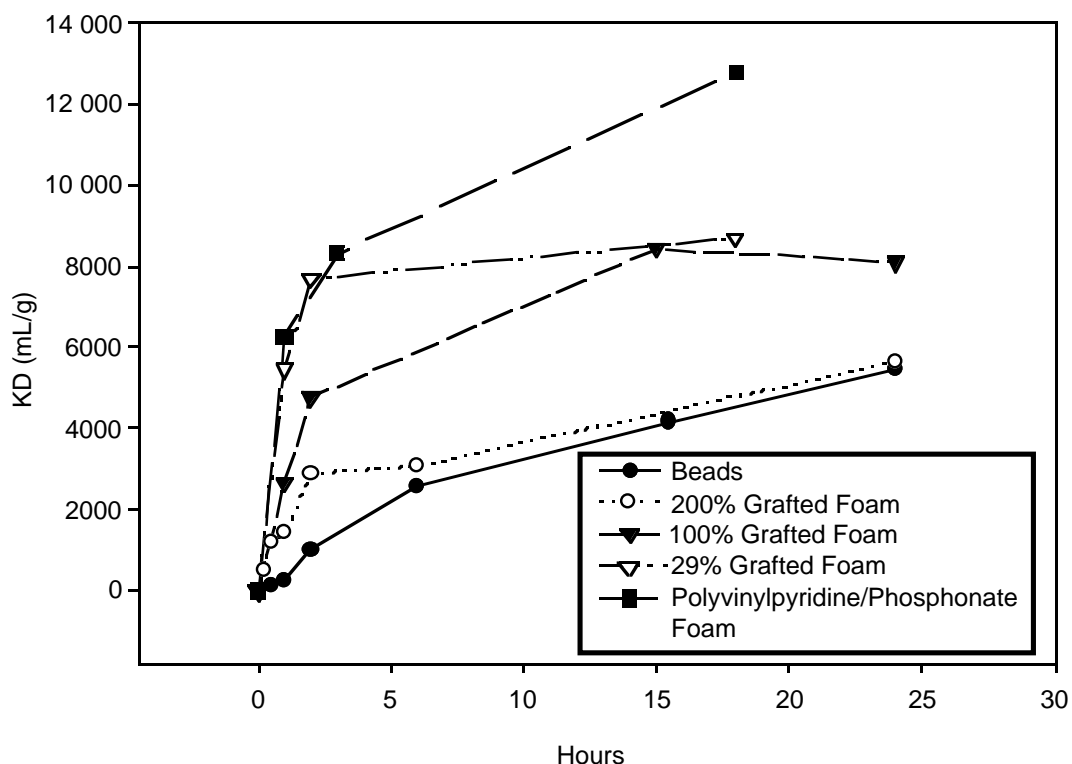


Fig. 10. Fe Uptake from 10-N HCl.

30% to 200% weight gain were obtained. We prepared the polyvinylpyridine/polyvinylphosphonate ester grafted foam in a similar manner. Plutonium uptake studies using the grafted foams are in progress, and we will report results in the second quarter of fiscal year 1997.

The contract with Dr. Spiro Alexandratos at the University of Tennessee has been arranged, with work to start in early January 1997.

Dr. Alexandratos will investigate foams functionalized with mono- and diphosphonate ligands at various degrees of cross-linking.

Dr. Alexandratos will use the ligands shown in Fig. 11. to functionalize the foams with the optimum degree of cross-linking. Dr. Alexandratos will test the functionalized foams for Eu(III) and Fe(III) uptake and send the most promising to Los Alamos for plutonium studies.

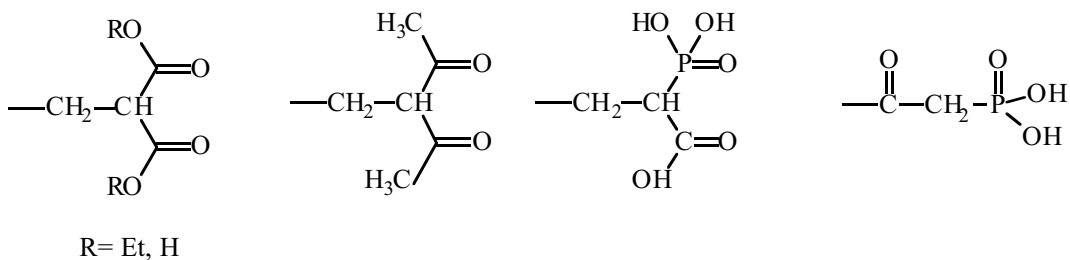


Fig. 11. Ligands used by University of Tennessee researchers to functionalize foams for study of Eu(III) and Fe(III) uptake.

Core Technology:
Materials Science—Thermodynamics

Principal Investigator: Mark A. Williamson

Task Description. The objective of this research is to study the vaporization chemistry, thermodynamics, and phase behavior of plutonium and americium oxychlorides. These species are of interest to researchers working on the salt distillation effort. If complete oxidation of plutonium and americium chlorides does not occur, oxychlorides could be present in the salt matrices that are to be treated by the distillation process. The data collected in this study can be used to better understand and model the distillation process.

Status/Accomplishments. Research activities for the first quarter of fiscal year 1997 (FY97) included (1) mass spectrometer calibration experiments and (2) vaporization studies of plutonium oxychloride.

Mass Spectrometer Calibration

Experiments. Researchers at Los Alamos National Laboratory completed two types of mass spectrometer calibration experiments. First, we determined the sensitivity of the mass spectrometer by measuring the temperature dependence of the intensity of uranium tetrafluoride. The sensitivity of the mass spectrometer is determined from the uranium tetrafluoride intensity-temperature product and the known vapor pressure of uranium tetrafluoride.¹ We

calculated the sensitivity constant to be (0.074 ± 0.007) atm/A K. A useful check on the validity of the uranium tetrafluoride vaporization data is a comparison of the enthalpy of vaporization obtained in this study with that reported in the literature. The enthalpy of vaporization was calculated in this study to be (310.6 ± 9.2) kJ/mole, and that reported in the literature is (313.8 ± 2.1) kJ/mole.¹

Second, we calibrated the electron energy scale of the mass spectrometer by collecting the ionization efficiency curve for uranium tetrafluoride and its fragment ions. The curve for the parent ion, uranium tetrafluoride, at 887 K is given in Fig. 12. The appearance potential for uranium tetrafluoride is 10.32 eV.² The difference between the literature value and that obtained from the curve in Fig. 12 is the energy scale correction, -4.3 eV.

Vaporization Studies of Plutonium Oxychloride.

We studied the vaporization chemistry of plutonium oxychloride in the temperature range 1125 K–1250 K. The vapor species observed were plutonium oxychloride, plutonium trichloride, and perhaps plutonium monochloride. Ionization efficiency curves were obtained for each of the parent ions and their

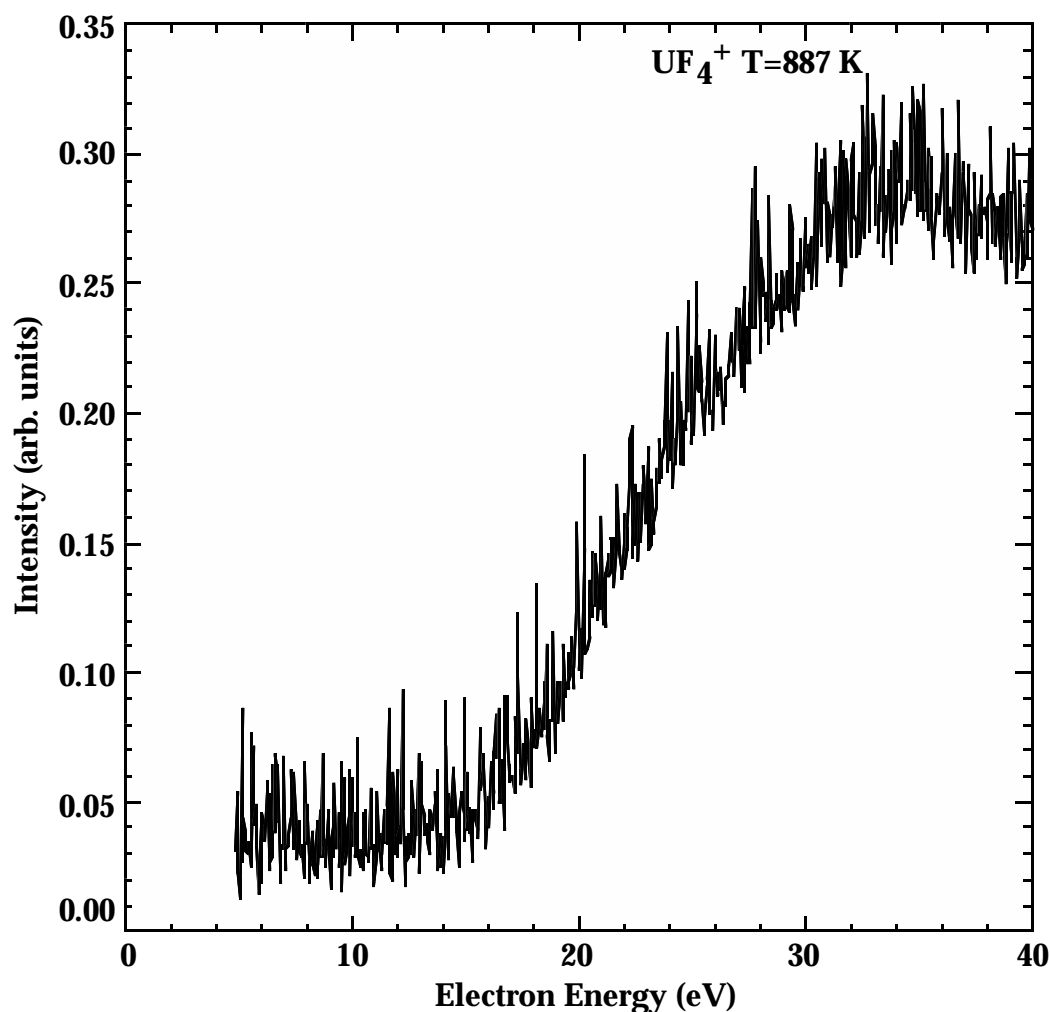


Fig. 12. Ionization efficiency curve for uranium tetrafluoride at 887 K.

fragment species. The curve for plutonium oxychloride is given in Fig. 13. This is the first reported curve for plutonium oxychloride. The energy-corrected appearance potential will be deduced from this curve and that for uranium tetrafluoride. We will treat the data for plutonium trichloride and monochloride similarly.

For each of the vapor species, we also collected temperature dependence of intensity data. These data will be used to calculate the thermodynamic properties associated with the vaporization processes.

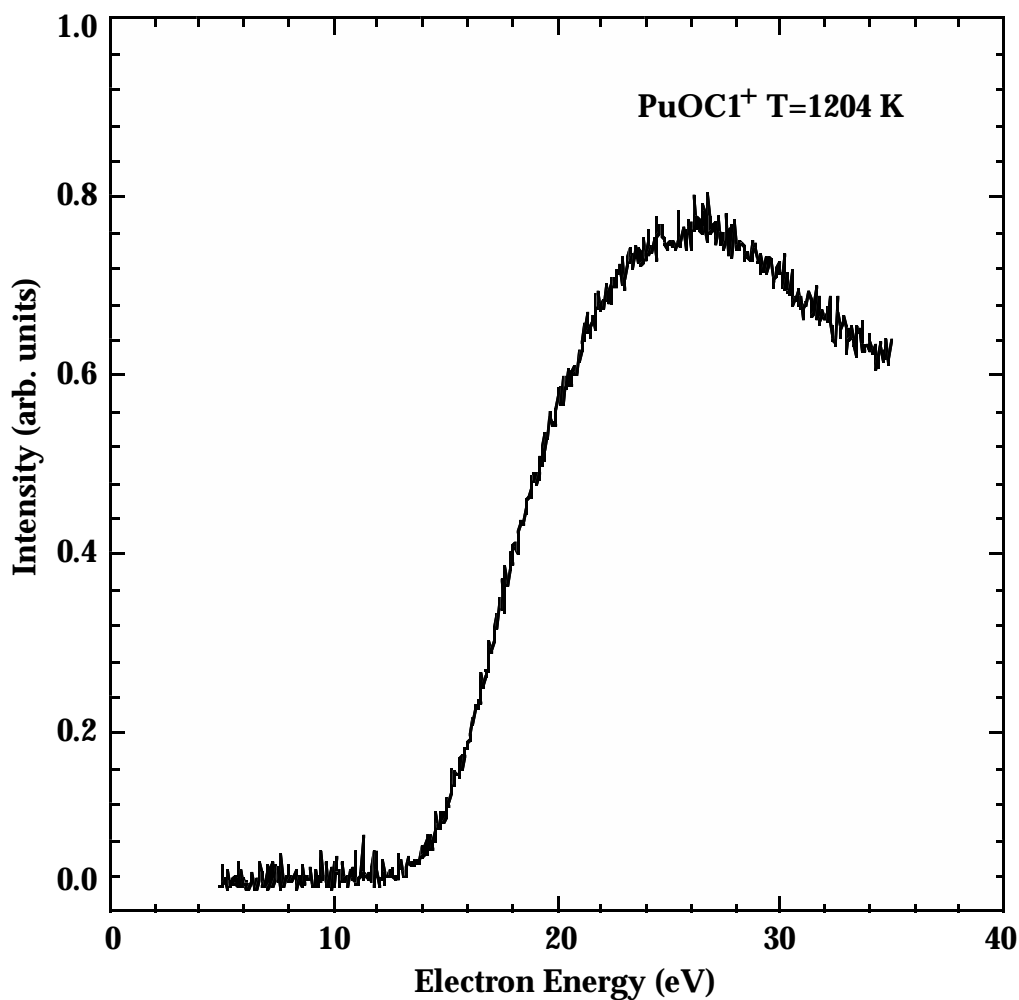


Fig. 13. Ionization curve for plutonium oxychloride at 1204 K.

References

1. D. L. Hildenbrand, *J. Chem. Phys.* **66**(11), 4788 (1977).
2. D. L. Hildenbrand, L. V. Gurvich, and V. S. Yungman, "The Chemical Thermodynamics of Actinide Elements and Compounds—Part 13, The Gaseous Actinide Ions," (IAEA, Vienna, 1983).

Core Technology:
Materials Science—Mineral Waste Forms

Principal Investigator: John Y. Huang

Task Description. Plutonium-containing zircon (Pu-zircon) is used to enhance the rate of solid-state reactions. Large-scale fabrication of Pu-zircon, which involves high temperatures and pressures, requires development of containment systems that can withstand such severe conditions.

Status/Accomplishments. During the first quarter of fiscal year 1997, Los Alamos National Laboratory researchers used the synthesis of nonradioactive zircon to test the performance of a containment system that has high melting temperature, is compressible under high pressure, and is chemically inert to the reaction mixture. This containment system consists of an inner quartz container in contact with reactants, a special sealant that joins the quartz container parts without the use of hydrogen/oxygen flames inside gloveboxes, and a welded tantalum outer container.

We load approximately 80-g batches of zirconia and quartz powders in equimolar ratios into the containers. The materials are processed in a hot isostatic press at temperatures between 1450°C and 1500°C and at pressures ranging from 4000 to 10 000 pounds per square inch (psi) for time intervals between 2 to 8 h. Fig. 14 shows temperature and pressure as a

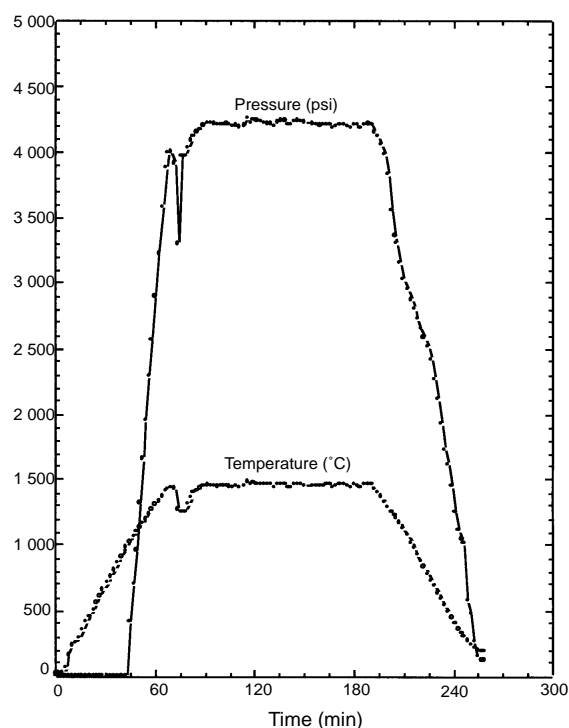


Fig. 14. Temperature and pressure profiles for run # hip-1.

function of time for one of the processing runs.

We took samples from the product and subjected them to x-ray powder diffraction analyses in order to determine the extent of reaction. Fig. 15 indicates that after 2 h of processing at 1450°C and 4000 psi, a significant amount of zircon has been formed from zirconia and quartz, even though the reaction is not complete. Reaction between the inner quartz and the outer tantalum containers is

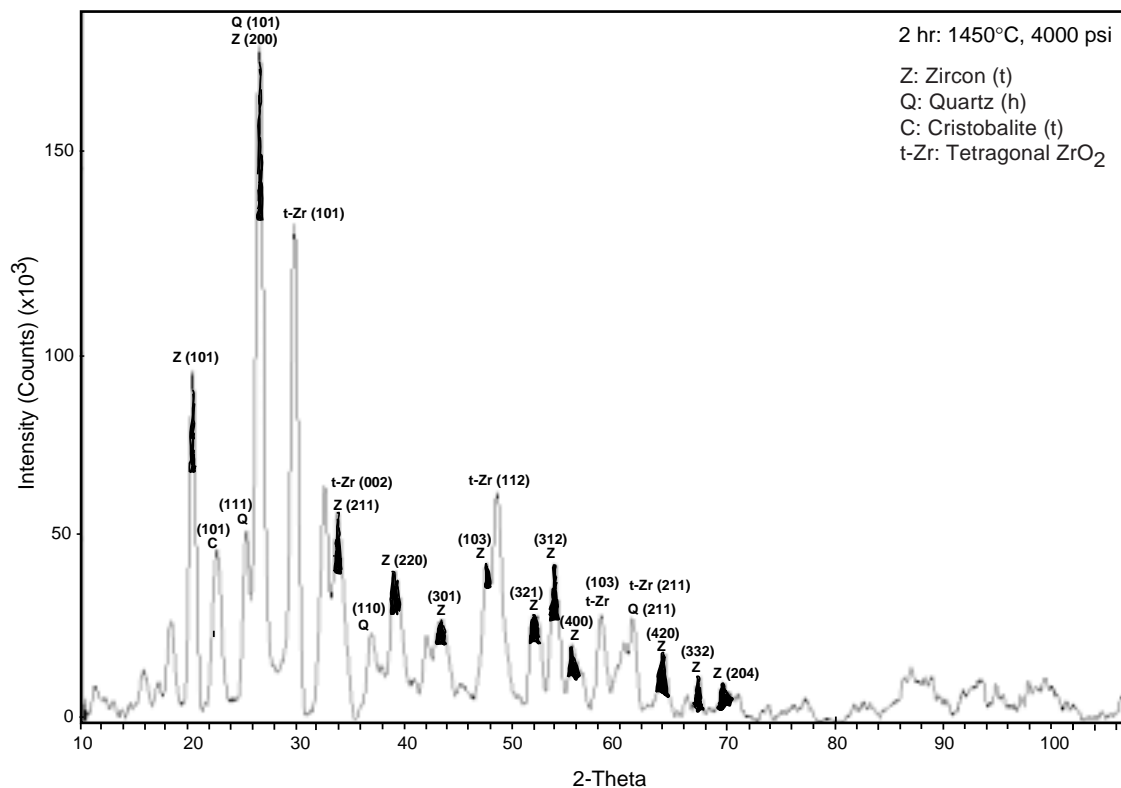


Fig. 15. X-ray powder diffraction pattern for material processed at 1450°C and 4000 psi for 2 hours. The peaks labeled Z are due to zircon, the product; the other peaks, labeled Q (quartz), t-Zr, (tetragonal zirconia), and C (cristobalite), are due to the reactants.

evident. We are performing further work to understand and to prevent the interactions between various components of the containment system so that Pu-zircon can be safely processed without release of contamination.

Core Technology:

Synthesis and Structural Characterization of Plutonium(IV) and Plutonium(VI) Phosphates

Principal Investigators: Wolfgang H. Runde and D. Kirk Veirs

Task Description. Phosphate coordination plays a significant role in actinide chemistry and can be used to stabilize plutonium. Among the concepts for underground storage of high-level radioactive waste, phosphate minerals are considered as potential secondary barriers or backfill materials to reduce actinide solubility and to enhance adsorption of radionuclides in a nuclear waste repository. Phosphate minerals are well suited to such purposes because of their high affinity for actinides and the low solubility of actinide phosphate minerals in ground water.

Despite the importance of actinide phosphate compounds, surprisingly little is known about their structure, bonding, stability, and spectroscopic properties. Synthetic compounds studied to date have been obtained by precipitation of actinide ions from aqueous solution under atmospheric conditions. The compounds can be grouped into two general categories: (1) binary phases described by varying ratios of actinide (or actinyl) and phosphate and (2) ternary phases described by varying ratios of actinide (or actinyl), phosphate and M , where M is an alkali or alkaline-earth ion.

Although only two plutonium phosphate structures have been fully characterized, the structural and

chemical diversity within these compounds is quite remarkable. This diversity arises from the various actinide coordination numbers (6 to 9) and oxidation states (+III to +VI) and from the η^1 and η^2 binding modes of the phosphate ligands that occupy lattice sites to generate one-, two-, and three-dimensional frameworks. These varying structural properties will influence a wide range of physical properties such as solubility, leachability, and radiation resistance.

The objective of Los Alamos National Laboratory researchers is to develop a fundamental understanding of plutonium phosphate chemistry, which will enable synthesis of plutonium phosphate compounds and characterization of solid-state and chemical behavior under radiolysis and aqueous conditions. Well-characterized plutonium phosphate compounds produced in this work can be used for plutonium solubility studies.

Status/Accomplishments. Initial efforts focus on the synthesis and structural characterization of solid Pu(VI) phosphates. We have performed scoping experiments with uranium in the +VI oxidation state. Solid compounds in the $\text{UO}_2(\text{NO}_3)_2\text{-H}_3\text{PO}_4$ and $\text{UO}_2(\text{NO}_3)_2\text{-H}_3\text{PO}_4\text{-HNO}_3$ systems, prepared by precipitation

from aqueous solutions, have been characterized by powder x-ray diffraction. The compounds, $(\text{UO}_2)_3\text{PO}_4$ and $\text{UO}_2\text{HPO}_4 \cdot x\text{H}_2\text{O}$, are highly crystalline when freshly precipitated. We will characterize these compounds with synchrotron radiation at the Stanford Linear Accelerator Center in early January 1997.

Publication

H. T. Hawkins, B. E. Scheetz, and G. D. Guthrie, Jr., "Preparation of Monophasic [NZP] Radiophases: Potential Host Matrices for the Immobilization of Reprocessed Commercial High-Level Wastes," Los Alamos National Laboratory report LA-UR-96-3897 (to be published in *Scientific Basis for Nuclear Waste Management*, proceedings of the 1996 Materials Research Society Symposium of the Scientific Basis for Nuclear Waste Management, Boston, Massachusetts, December 2–6, 1996).

Core Technology:
Plutonium Phosphate Solution Chemistry

Principal Investigator: David G. Karraker, Savannah River Site

Task Description. An attractive process for the destruction of glovebox waste involves oxidation of organic material by nitric acid or hydrogen peroxide in a concentrated phosphoric acid solution. After oxidation of organic matter, plutonium and other metal ions will accumulate in the phosphoric acid. This study of the chemistry of plutonium in concentrated phosphoric acid is aimed at determining the properties of plutonium in strong phosphoric acid and investigating methods for recovering plutonium and recycling H_3PO_4 .

Status/Accomplishments. Researchers at Savannah River Site previously measured the absorption spectra of Pu(III) and Pu(IV) in 85% (14.6 M) H_3PO_4 and prepared standard curves of absorbance versus concentration. The solubility of both Pu (III) and Pu(IV) in 85% H_3PO_4 was found to be at least 170 g/mL.

X-ray diffraction patterns of the blue solid in equilibrium with concentrated Pu(III) solution have identified the solid as PuPO_4 . The solid phase in equilibrium with the pink Pu(IV) solution has been identified as $\text{Pu}(\text{PO}_3)_4$. Presumably, this compound arises by dehydration of $\text{Pu}(\text{H}_2\text{PO}_4)_4$. X-ray patterns of the plutonium oxalate-phosphate did not identify its

composition. Bjorklund¹ found that the mixed oxalate-phosphate has a variable composition.

Our attempts to coprecipitate a plutonium phosphate with boric acid, calcium phosphate, or Fe(III) phosphate were unsuccessful. Plutonium was not absorbed from 85% H_3PO_4 solution on anion resin, even though it appears probable that the plutonium species in this solution is an anion complex.

Our attempts to vacuum-distill H_3PO_4 with a 140°C pot temperature succeeded only in removing water, which raised 85% acid to 98%, as determined by density measurements. The condensed overheads were pH 5 water. At higher pot temperatures, corrosion by H_3PO_4 became extreme. A TeflonTM stirrer dissolved in the hot acid, and the PyrexTM vessel was severely etched. The overheads from this distillation attempt were 0.1 M acid.

Future plans include attempts to coprecipitate plutonium from strong H_3PO_4 solution by using dibasic organic acids such as succinic, maleic, ophthalic, and salicylic acids.

Reference

1. Carl W. Bjorklund, *J. Am. Chem. Soc.* **79**, 6347–6350 (1958).

Core Technology:
Molten Salt/Nonaqueous Electrochemistry

Principal Investigator: Wayne H. Smith

Task Description. The purpose of this work is to fully characterize the chemical behavior of actinide elements in room-temperature molten-salt solvent systems. This characterization will enable a deeper understanding of the fundamental properties of selected actinide elements such as uranium, plutonium, americium, thorium, and neptunium. Enhanced understanding of actinide properties will have direct applications to the development of advanced actinide purification and separation schemes.

Status/Accomplishments. This is a new-start project for fiscal year 1997. During the first quarter of fiscal year 1997, we interviewed and selected a postdoctoral candidate to work on the project. He is available to join us on March 1, 1997. We also procured chemicals and equipment and found a location at which to carry out the project. Experimentation is set to begin in January 1997.

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